

RETARDERS FOR CONCRETE, AND THEIR
EFFECTS ON SETTING TIME AND
SHRINKAGE

DECEMBER 1972 — NUMBER 51



BY

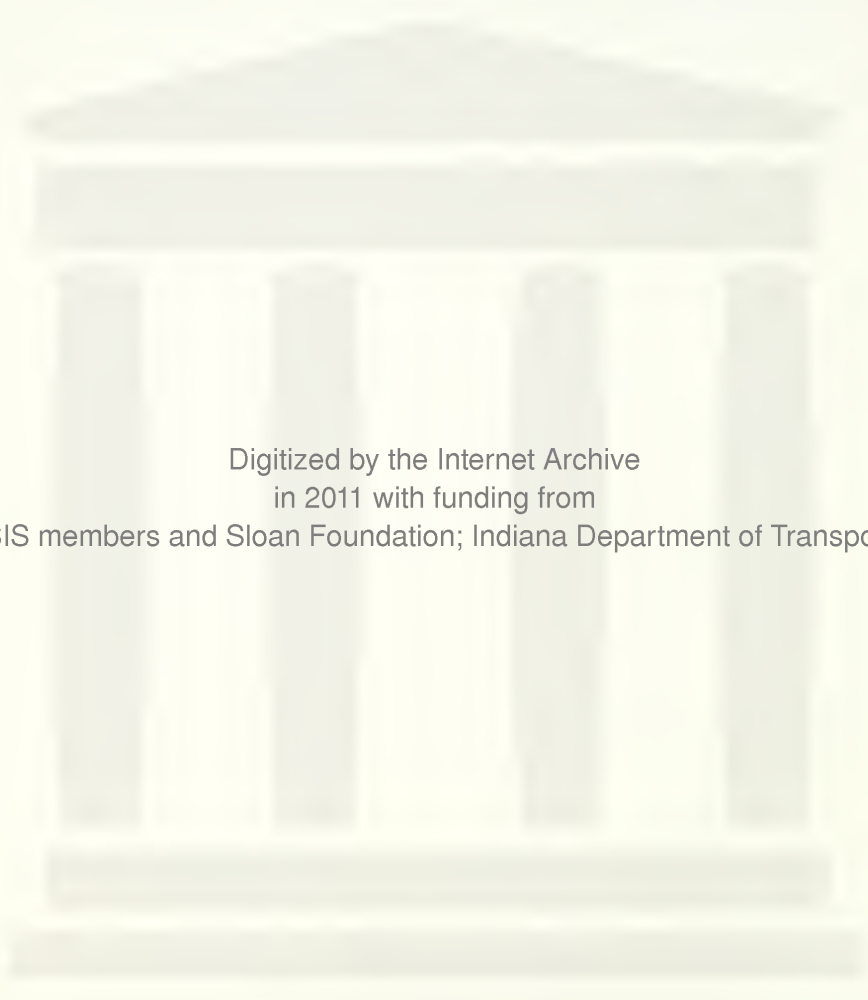
YASUHIKO YAMAMOTO

JHRP

JOINT HIGHWAY RESEARCH PROJECT
PURDUE UNIVERSITY AND
INDIANA STATE HIGHWAY COMMISSION



1. Report No.	2. Government Accession No.	3. Recipient's Catalog No.	
4. Title and Subtitle RETARDERS FOR CONCRETE, AND THEIR EFFECTS ON SETTING TIME AND SHRINKAGE		5. Report Date December 1972	6. Performing Organization Code
7. Author(s) Yasuhiko Yamamoto		8. Performing Organization Report No. JHRP-51-72	
9. Performing Organization Name and Address Joint Highway Research Project Civil Engineering Building Purdue University West Lafayette, Indiana 47907		10. Work Unit No.	11. Contract or Grant No. HPR-1(10) Part II
12. Sponsoring Agency Name and Address Indiana State Highway Commission 100 N. Senate Avenue Indianapolis, Indiana 46204		13. Type of Report and Period Covered Interim Report	
15. Supplementary Notes Prepared in cooperation with Federal Highway Administration and U. S. Department of Transportation		14. Sponsoring Agency Code	
16. Abstract Sixty-five pure chemicals and three proprietary retarders were tested in the penetration test for setting time at concentrations at or around 0.1% of the cement. The most effective retarders had several, closely-grouped oxygen atoms in hydroxyl, carboxyl, or carbonyl groups. Some of the retarders were used in the fabrication of 0.2 x 0.2 x 4-in. bars of cement paste, which were subsequently oven-dried and the shrinkage, non-evaporable water content, and specific surface of the paste was determined. The retarders caused a change in the shrinkage that was paralleled by a change in the specific surface of the paste.			
* The contents do not necessarily reflect the official views or policies of the Federal Highway Administration. This report does not constitute a standard, specification, or regulation.			
17. Key Words Concrete, retarders, shrinkage, microstructure		18. Distribution Statement The contents of this report reflect the views of the author who is responsible for the facts and the accuracy of the data presented herein.*	
19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages 181	22. Price



Digitized by the Internet Archive
in 2011 with funding from
LYRASIS members and Sloan Foundation; Indiana Department of Transportation

RETARDERS FOR CONCRETE, AND THEIR EFFECTS ON SETTING TIME AND SHRINKAGE

File: 4-6-12

C. F. Scholer
M. B. Scott
J. A. Spooner
N. W. Steinkamp
H. R. J. Walsh
E. J. Yoder

Interim Report
RETARDERS FOR CONCRETE, AND THEIR EFFECTS ON SETTING
TIME AND SHRINKAGE

by

Yasahiko Yamamoto
Graduate Instructor in Research

Joint Highway Research Project

Project No.: C-36-47L

File No.: 4-6-12

Prepared as Part of an Investigation

Conducted by

Joint Highway Research Project
Engineering Experiment Station
Purdue University

in cooperation with the

Indiana State Highway Commission

and the

U.S. Department of Transportation
Federal Highway Administration

The contents of this report reflect the views of the author who is responsible for the facts and the accuracy of the data presented herein. The contents do not necessarily reflect the official views or policies of the Federal Highway Administration. This report does not constitute a standard, specification, or regulation.

Purdue University
West Lafayette, Indiana
December 28, 1972

ACKNOWLEDGEMENTS

The writer wishes to express deep appreciation to his major professor, Dr. W. L. Dolch, for his kind guidance and understanding during the course of this work. Dr. S. Diamond and Dr. C. F. Scholer should be also appreciated for their valuable suggestions and helps.

The discussion with Mr. D. N. Winslow was helpful and meaningful in solving many difficulties. Some technical phases of this work were done by the assistance of Mrs. T. R. Brendel. The writer is thankful to them and also to many other people who have helped him in many respects toward the accomplishment of this work.

This research was sponsored by the Indiana Highway Department and administrated by Joint Highway Research Project of Purdue University. The writer wishes to thank the authorities for the support of this work.

Finally, the writer is thankful to Dr. M. Kokubu and Dr. H. Okamura, professor and associate professor, respectively, University of Tokyo, Japan, for their continuous encouragement in pursuing the advanced degree in the United States.

TABLE OF CONTENTS

	Page
LIST OF TABLES	vii
LIST OF FIGURES	viii
ABSTRACT	xiii
CHAPTER I - INTRODUCTION	1
CHAPTER II - REVIEW OF LITERATURE	6
Interaction of Retarder with Cement	6
Effective Molecular Structure of Retarder and Retardation Mechanism	13
Drying Shrinkage of Paste, Mortar, and Concrete as Affected by Retarders	17
CHAPTER III - MATERIALS	21
Admixtures	21
Cement	27
Sand	29
Water	29
CHAPTER IV - EXPERIMENTAL WORK	30
A - Setting Time Measurements	30
General Remarks	30
Apparatus	31
Container	31
Penetration Resistance Apparatus	31
Mixer	31
Preparation of Mortar Specimens	33
Mixing Proportions and Size of Batch	33
Mixing Procedures	33
Casting and Storage of Specimens	34
Penetration Test Procedure	34

TABLE OF CONTENTS, cont.

	Page
B - Measurement of Shrinkage of Cement Pastes . . .	35
General Considerations	35
Apparatus	36
Mold for Cement Paste Specimens	36
Gauge Studs and Length Comparator	36
Mixing Apparatus	38
Preparation of Cement Paste Specimens	40
Mixing Proportion and Concentration of Retarders	40
Mixing, Casting, and Curing of Cement Paste Specimens	42
Measurements of Length and Weight, Method of Drying	44
C - Determination of Degree of Hydration of Cement Pastes	46
Loss on Ignition Test	46
Derivation of Equations for Determining Non-Evaporable Water and Evaporable Water	47
Assumptions	47
Notation	48
Derivation of Equations	50
Reduction of Data	51
D - Surface Area Measurements of Cement Pastes . .	52
General Remarks	52
Apparatus and Procedures of Measurement	53
E - Scanning Electron Microscope Observation . . .	54
General Procedures	54
CHAPTER V - RESULTS	56
Infrared Spectra of Commercial Retarders	56
Non-Evaporable Water Content of Fully Hydrated Cement Paste	56
Result of Setting Time Experiments	59
Commercial Retarders	59
Pure Chemicals	66
Effects of Retarders on the Drying Shrinkage of Cement Paste at Various Stages of Hydration . .	72

TABLE OF CONTENTS, cont.

	Page
Drying Shrinkage of Mature Cement Pastes When Dried at 50% Relative Humidity	79
Water Content of Cement Pastes	84
Specific Surface Area of Cement Pastes	87
Scanning Electron Microscopy of Cement Pastes	96
CHAPTER VI - DISCUSSION	109
Molecular Structure of Retarders	109
Effect of Retarders on the Hydration of Cement	128
Effect of Retarders on the Shrinkage of Cement Pastes	143
CONCLUSIONS	153
LIST OF REFERENCES	155
APPENDICES	
Appendix A: Correction Curve for Warping of Cement Paste Bars	161
Appendix B: Summary of Setting Time Experiments When Pure Chemicals Were Added	163
Appendix C: Shrinkage of Vacuum Oven-Dried Cement Pastes at Various Stages of Cement Hydration	169
VITA	181

LIST OF TABLES

Table	Page
1. List of Chemicals	22
2. List of Commercial Retarders	27
3. Composition and Properties of Lab Cement No 319	28
4. Concentration of Retarders Added to Cement Pastes	41
5. Non-Evaporable Water Content of Bottle Hydrated Cement (W/C = 10)	58
6. Summary of Relative Initial Setting Time of Mortars When Pure Chemicals Were Added	67
Appendix	
Tables	
7. Summary of Relative Setting Time of Mortar Samples When Pure Chemicals Were Added	164

LIST OF FIGURES

Figure		Page
1.	Calibration Curve for Proctor Penetrometer (ASTM C403)	32
2.	Mold for Cement Paste Specimens, Cement Paste Sample, and Paste Caster	37
3.	Length Comparator	39
4.	Apparatus for Drawing Mixing Solution from Funnel into Mixing Container	43
5.	Schematic Diagrams of Cement and Cement Paste .	49
6.	Infrared Spectra of Commerical Retarders . . .	57
7.	Penetration Resistance vs Elapsed Time for Mortar with Retarder L	60
8.	Penetration Resistance vs Elapsed Time for Mortar with Retarder A	61
9.	Penetration Resistance vs Elapsed Time for Mortar with Retarder S	62
10.	Effect of Concentration of Retarder L on Setting Time of Mortar	63
11.	Effect of Concentration of Retarder A on Setting Time of Mortar	64
12.	Effect of Concentration of Retarder S on Setting Time of Mortar	65
13.	Penetration Resistance vs Elapsed Time for Mortar with 1,3-Dihydroxy-2-Butanone	73
14.	Concentration of Admixture vs Relative Initial Setting Time of Mortar (No. 1)	74
15.	Concentration of Admixture vs Relative Initial Setting Time of Mortar (No. 2)	75

LIST OF FIGURES, cont.

Figure	Page
16. Shrinkage of Vacuum Oven-Dried Cement Pastes at Various Stages of Hydration (Commercial Retarders)	76
17. Shrinkage of Vacuum Oven-Dried Cement Pastes at Various Stages of Hydration (Pure Chemicals)	77
18. Shrinkage vs Drying Time for Mature Cement Pastes When Dried at 50% Relative Humidity (Commercial Retarders)	80
19. Shrinkage vs Drying Time for Mature Cement Pastes When Dried at 50% Relative Humidity (Pure Acid Chemicals)	81
20. Shrinkage vs Weight Loss of Mature Cement Pastes When Dried at 50% Relative Humidity (Commercial Retarders)	82
21. Shrinkage vs Weight Loss of Mature Cement Pastes When Dried at 50% Relative Humidity (Pure Acid Chemicals)	83
22. Non-Evaporable Water vs Evaporable Water of Cement Pastes (Commercial Retarders)	85
23. Non-Evaporable Water vs Evaporable Water of Cement Pastes (Pure Chemicals)	86
24. Non-Evaporable Water vs Curing Age of Cement Pastes (Commercial Retarders)	88
25. Non-Evaporable Water vs Curing Age of Cement Pastes (Pure Chemicals)	89
26. Specific Surface Area of Vacuum Oven-Dried Cement Pastes When Expressed on the Basis of Total Ignited Weight of Sample (No. 1)	90
27. Specific Surface Area of Vacuum Oven-Dried Cement Pastes When Expressed on the Basis of Total Ignited Weight of Sample (No. 2)	91
28. Specific Surface Area of Hydrated Portion of Vacuum Oven-Dried Cement Pastes (Commercial Retarders)	93

LIST OF FIGURES, cont.

Figure	Page
29. Specific Surface Area of Hydrated Portion of Vacuum Oven-Dried Cement Pastes (Pure Chemicals - No. 1)	94
30. Specific Surface Area of Hydrated Portion of Vacuum Oven-Dried Cement Pastes (Pure Chemicals - No. 2)	95
31. Unhydrated Cement Grains (X5000)	97
32. Cement Paste With No Admixture (X3000), Age: 1 min	97
33. Cement Paste With No Admixture (X9000), Age: 1 min	98
34. Cement Paste With Calcium Lignosulfonate (X5000), Age: 1 min	98
35. Cement Paste With Citric Acid (X3000), Age: 1 min	99
36. Cement Paste With Sucrose (X5000), Age: 1 min	99
37. Cement Paste With No Admixture (X5000), Age: 5 min	101
38. Cement Paste With Calcium Lignosulfonate (X5000), Age: 5 min	101
39. Cement Paste With Citric Acid (X3000), Age: 5 min	102
40. Cement Paste With Sucrose (X5000), Age: 5 min	102
41. Cement Paste With Citric Acid (X3000), Age: 10 min	103
42. Cement Paste With Citric Acid (X8000), Age: 10 min	103
43. Cement Paste With Citric Acid (X3000), Age: 30 min	104

LIST OF FIGURES, cont.

Figure	Page
44. Cement Paste With Citric Acid (X3000), Age: 1 hr	104
45. Cement Paste With No Admixture (X5000), Age: 1 hr	106
46. Cement Paste With Sucrose (X3000), Age: 30 min	106
47. Cement Paste With No Admixture (X2000), Age: 12.5 hr (degree of hydration: 24%)	107
48. Cement Paste With Glycolic Acid (X2000), Age: 15.5 hr (degree of hydration: 26%)	107
49. Cement Paste With Retarder A (X2000), Age: 14 hr (degree of hydration: 18%)	108
50. Cement Paste With Retarders (X2000), Age: 13 hr (degree of hydration: 20%)	108
51. Retardation Ability vs Complexing Ability of Chemicals	135
52. Effect of Continuous Vacuum Oven-Drying on Shrinkage of Cement Pastes	145
53. Effect of Continuous Vacuum Oven-Drying on Weight Loss of Cement Pastes	146
Appendix Figures	
54. Correction Curve for Warping of Cement Paste Bars	162
55. Shrinkage of Vacuum Oven-Dried Cement Pastes at Various Stages of Cement Hydration (No Admixture)	170
56. Shrinkage of Vacuum Oven-Dried Cement Pastes at Various Stages of Cement Hydration (Retarder L)	171
57. Shrinkage of Vacuum Oven Dried Cement Pastes at Various Stages of Cement Hydration (Retarder A)	172

LIST OF FIGURES, cont.

Figure	Page
58. Shrinkage of Vacuum Oven-Dried Cement Pastes at Various Stages of Cement Hydration (Retarder S)	173
59. Shrinkage of Vacuum Oven-Dried Cement Pastes at Various Stages of Cement Hydration (Glycolic Acid)	174
60. Shrinkage of Vacuum Oven-Dried Cement Pastes at Various Stages of Cement Hydration (Sucrose)	175
61. Shrinkage of Vacuum Oven-Dried Cement Pastes at Various Stages of Cement Hydration (3-Hydroxy-2-Butanone)	176
62. Shrinkage of Vacuum Oven-Dried Cement Pastes at Various Stages of Cement Hydration (Hydroquinone)	177
63. Shrinkage of Vacuum Oven-Dried Cement Pastes at Various Stages of Cement Hydration ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$)	178
64. Shrinkage of Vacuum Oven-Dried Cement Pastes at Various Stages of Cement Hydration (Effect of Concentrations of Citric Acid) . . .	179
65. Shrinkage of Vacuum Oven-Dried Cement Pastes at Various Stages of Cement Hydration (effect of Water-Cement Ratio)	180

ABSTRACT

Yamamoto, Yasuhiko. Ph.D., Purdue University, December 1972. Retarders for Concrete, and Their Effects on Setting Time and Shrinkage. Major Professor: W. L. Dolch.

The main purposes of this work are to gain some insight into effective molecular structure of retarders and to examine the shrinkage behavior of cement pastes as affected by the addition of retarders.

A total of sixty five organic chemicals were tested for their retarding abilities by means of setting time experiment on mortar specimens by the penetration method. The chemicals were added mostly at the concentration of 0.1% of cement by weight. Three commercial retarders that are chemically classified in the three principal categories were also tested at several concentrations. The mix proportions of the mortars were kept constant; water-cement ratio and sand-cement ratio being 0.50 and 2.75, respectively. The effectiveness of the chemicals as retarders was judged by comparing the initial setting time of a sample with that of a control sample without the admixture. Effect of the concentration of admixture was studied for the commercial retarders and some chemicals. These results

were discussed in connection with the effective molecular configurations of retarders and possible retardation mechanisms.

Small cement paste bars (1/5 x 1/5 x 4 in.) were prepared for shrinkage measurements. Admixtures used in this part include five chemicals that were found to be retarders in this work, the three commercial retarders, and $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (accelerator). Concentration of each retarder was selected in such a way that it gave 50% of additional retardation compared with a control mortar. Water-cement ratio was fixed at 0.40. Drying of the samples was conducted in a vacuum oven at 105 to 110°C for 24 hours. Shrinkage was compared at various degrees of cement hydration; the ages of samples were as early as 10hr after mixing to 8 months, at which time 90% or more of the cement was hydrated.

Determinations of specific surface area, non-evaporable and evaporable water contents, and scanning electron microscopic observation were made on cement paste samples to explore whether or not some changes were induced in the cement hydrates by the addition of retarders.

The following are main findings in this research.

1. Hydroxyl, carbonyl, and carboxyl groups are all effective in retarder molecules. Strong retarder molecules contain many of these groups in such a way that the oxygen atoms are constrained to approach each other closely.

Substitution of other more weakly electronegative groups for these groups results in greatly reduced effectiveness.

2. Retarders cause a moderate increase in the shrinkage of cement pastes at ages when more than about half hydration is attained in about 4 days. At lesser ages the shrinkage may be increased or decreased.

3. When cement paste are severely dried of all their evaporable water, they exhibit shrinkage behavior that shows a minimum at about half hydration and a maximum earlier. A similar change is observed in the specific surface area of the hydrated cement. Some cause and effect relationship exists between these quantities.

CHAPTER I - INTRODUCTION

Retarders are classified as type B or type D chemical admixtures for portland cement concrete in ASTM Designation C494. Their primary function is, as the name implies, to retard the setting time of concrete. Many problems of hot weather concreting, mass concrete, multi-lift concreting, continuous placement, and others have been helped by the use of retarders (1, 2)*.

As a secondary effect, many retarders reduce the water requirement to produce a concrete of desired workability and produce a concrete of higher strength with equal cement content. Some retarders, additionally, produce many small air bubbles, much the same as those produced by air-entraining agents in concrete mixtures. Hence, the use of retarders is also beneficial to other properties of concrete such as workability, strength, and durability (3).

Commercial retarders are classified chemically into three categories:

1. lignosulfonic acids and their salts
2. hydroxycarboxylic acids and their salts
3. carbohydrates (sugars)

* Numbers in parenthesis refer to references at the end of this paper.

When these retarders are added to concrete mixtures, some kind of physical and/or chemical reaction takes place in such a way to retard the setting time. Little is known of what the effective molecular structures of the retarders are and how the retardation mechanism proceeds.

As will be shown in Chapter II, the most widely believed theory of the retardation mechanism is the so-called "coating theory". The idea of the theory is basically as follows: As soon as retarders are added they are adsorbed at the solid-water interface of cement grains or their hydration products. The sorbed retarder molecules block or delay further contact of the unhydrated cement with water and therefore retard the hydration of the cement.

The effective molecular structure of retarders, then, has to be of such a configuration that the coating is most efficiently attained. Most workers believe that large chain molecules with many hydroxyl groups are essential to effective retarders. The -OH groups are for bonding with cement grains, presumably by hydrogen bonding to surface oxygen atoms.

However, owing to the variety of both the compounds in portland cement and molecular structures of retarders, it is difficult to imagine that the theory mentioned above is the only mechanism for the retardation.

Some workers have reported that retarders increase the shrinkage of concrete (4). On the other hand, other

workers observed no increase in shrinkage with the addition of retarders (3). Because the shrinkage behavior of concrete is extremely complex and is influenced by many factors, it is not surprising to see this discrepancy. Yet, it is of importance to establish basic information as to whether retarders really change the shrinkage behavior of concrete and, if they do, how much the change is and how it should be considered in practice. If sound aggregates are used in concrete, change in shrinkage behavior of the concrete can be attributed to that of the cement paste in the concrete. Therefore a detailed study on cement paste should provide such information.

Hardened cement paste consists of capillary pores, cement gel, and unhydrated cement grains (5). Each of them has a certain role in the shrinkage behavior of cement paste. The extent to which these phases exist and, therefore, the structure of the cement paste depends on the degree of hydration. Since retarders change the rate at which a cement hydrates, a consideration of the magnitude of these phases is appropriate when drying shrinkage of retarded cement paste is compared with that of unretarded paste.

Additionally, there is evidence that the morphology of hydrated C_3A^* is altered significantly by the addition of

* The usual abbreviations are used through the paper:
 $C = CaO$, $S = SiO_2$, $A = Al_2O_3$, $H = H_2O$.

lignosulfonate, a constituent of some retarders (6). So there is some possibility that retarders also change the specific surface or crystal habit of the hydration products of cement paste and thereby induce different shrinkage behavior of the paste.

Hence, what seems important and necessary is to examine the effect of retarders on the structure of the hydration products at various hydration stages and to interpret the observed shrinkage behavior of cement pastes in these terms.

An alternate hypothesis, based on the coating theory, is that retarders act merely by changing the rate of, or time of initiation of, the hydration reaction. A combination of the kinetic and the structural change theories is, of course, also possible.

The present paper discusses the results of experiments undertaken to gain information on the action of retarders. By means of setting time experiments on mortar specimens, many chemicals were examined for their effects as retarders. Possible effective molecular structures of retarder molecules are discussed. Small cement paste bars were made with and without retarders. Their shrinkages were measured. The results are compared at various degrees of hydration of the cement, ranging from as early as 10 hours after mixing with water to 8 months of age, at which time the pastes were almost mature.

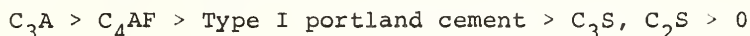
Determination of evaporable and non-evaporable water contents, measurement of specific surface area, and scanning electron microscopic observations were conducted to examine the properties and the structure of the cement pastes.

CHAPTER II - REVIEW OF LITERATURE

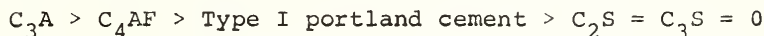
Interaction of Retarder with Cement

Blank, Rossington and Weinland (7) observed that the adsorption from aqueous solutions of salicylic acid and calcium lignosulfonate on C_2S and C_3S was negligibly small and showed the following order of the adsorption on the cement compounds from aqueous solution in 10 to 15 minutes.

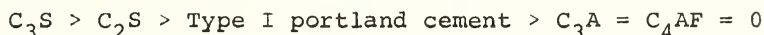
calcium lignosulfonate:



salicylic acid:



The adsorption on the compounds from ethyl alcohol solution, however, was in the following order for salicylic acid:



From these results, they suggested that the negligible adsorption on C_2S and C_3S in aqueous solution is probably a result of the competitive adsorption of water, and that certain modified properties of cement due to admixture addition are a result of the preferential adsorption of the admixture by C_3A and C_4AF , thereby rendering them inactive and allowing the main cementing compounds (C_3S and C_2S) to control the hydration reaction.

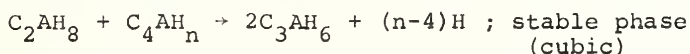
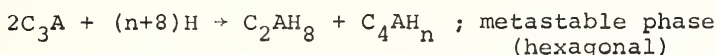
Seligmann and Greening (8) showed that one gram of C_3A could remove 99% of the sugar from 5 cc of a 1% sucrose solution within 7 minutes. The presence of gypsum or calcium hydroxide did not interfere. C_3A also sorbed considerable calcium lignosulfonate, whereas C_3S and C_4AF sorbed little. It may be added that a rough calculation using these results showed that the sugar adsorption on unhydrated C_3A corresponded to a uniform coverage of about 150 molecular layers. The result is unrealistic, and it would be adequate to suppose that the sucrose was adsorbed by the hydration products of C_3A instead of or in addition to the unhydrated material as Diamond (9) observed with salicylic acid.

Stein (10) observed that monomer organic anions exerted a relatively small influence on C_3S hydration, but a pronounced effect on C_3A hydration by forming calcium double salts with C_3A , similar to ettringite. Hansen (11) has a similar concept that the hydration of C_3A is retarded by chemisorbing, rather than adsorbing, lignosulfonate. The chemisorption results from the formation of double salts between the lignosulfonate and calcium ions in the surface of cement minerals.

Mielenz and Peppler (12), however, pointed out that formation of compounds isostructural with sulfoaluminates and containing such large anions as lignosulfonate would be impossible. They suggested that retardation of C_3A

hydration by materials like lignosulfonates may better be explained in terms of adsorption of lignosulfonate upon C_3A grains or precipitation of insoluble calcium lignosulfonate around the grains of C_3A .

The hydration of C_3A is widely believed to proceed in two steps in the absence of gypsum:



Daugherty and Kawalewski (13) examined the effect of many chemicals on the relative amount of hydration products of C_3A by quantitative x-ray diffraction analysis. They found that, in general, organic acids permitted the hydration of C_3A to proceed to C_3AH_6 while sugars and their derivatives blocked the hydration reaction at metastable C_2AH_8 and C_4AH_n . However, all the sugars and sugar derivatives examined accelerated the initial hydration of C_3A at the concentration level of 0.25 mole % relative to C_3A . They speculated on the retardation mechanism of C_3A hydration:

"In concentrations of 0.3 mole % or less relative to C_3A the organic materials complex or chelate with available calcium ions (and other cations) in solution and on the surface of the C_3A . These reactions might affect the rates of solution of C_3A and the solution, precipitation or nucleation of the hydration products in a manner which accelerates hydration.

After the available calcium is tied up, the organic material is adsorbed on the surface of C_3A . This adsorption may be chelation with calcium in the C_3A , complexation, or surface adsorption depending upon the type of organic molecule.....

Organic compounds with more insoluble calcium salts would be expected to form more closely packed, more impervious sheaths around the C_3A . This might prevent H_2O from further attacking the C_3A . The organic layers could prevent the intermediate products, C_2AH_8 and C_4AH_{13} , from transforming to C_3AH_6 . Retardation of hydration would be the result."

Young (6) made similar observation with lignosulfonate by measuring refractive indices of the hydration products of C_3A . Lignosulfonate stabilized C_4AH_{13} and C_2AH_8 with respect to C_3AH_6 . When gypsum was present, the formation of ettringite was not affected by the addition of lignosulfonate, and the final hydration products were low sulfoaluminate, C_2AH_8 , and C_4AH_{13} . Another interesting observation by Young is that there was no evidence of the transformation of C_2AH_8 and C_4AH_{13} to C_3AH_6 when C_3A , even in the absence of lignosulfonate, hydrated at low temperature, say less than $30^\circ C$.

Diamond (14, 15) analyzed salicylate bearing precipitates observed in the C_3A (or C_3AH_6) - salicylic acid-water system. They were amorphous salicylate-aluminum complexes and did not contain calcium.

Because the C_3A and C_3S phases in cement are responsible for early hydration of the cement, the papers introduced so far give an impression that the C_3A is mainly concerned with the retardation mechanism when retarders are added. Forbrich (16), however, demonstrated that salicylic acid delayed the time of maximum heat generation due to hydration of C_3S by 8 to 10 hr relative to a reference mixture,

and that calcium lignosulfonate shifted the peak more than 27 hours. On the other hand, the hydration of C_3A with 12% gypsum interground was accelerated by the addition of salicylic acid, but was retarded remarkably when calcium lignosulfonate was added.

Polivka and Klein (17) examined the setting time of many cements influenced by various admixtures and showed that retarders are more effective when used with cements of low alkali and low C_3A . Forbrich (16) also showed that cements low in C_3A and high in C_3S were the ones retarded to the greatest degree by either calcium lignosulfonate or salicylic acid.

Bruere (18) showed that delayed addition of retarders (citric acid and calcium lignosulfonate) produced a considerably longer setting time of cement paste. This effect was much greater in pastes made from ordinary portland cement, which had a high C_3A content, than in pastes made from low heat cement, which had a low C_3A content. Dodson and Farkas (19) observed the same result. Bruere suggested that this effect was due to competition between the gypsum in the cement and organic retarders to combine with or adsorb on C_3A surfaces and explained further:

"When cement is pre-mixed with water for a few minutes, gypsum has ample time to dissolve and coat the C_3A . Consequently, when the retarder is added to the pre-mixed paste, the C_3A is unable to adsorb it and a large amount of retarder is available to retard the silicate hydration reactions."

Seligmann and Greening (8) examined the effects of sucrose and lignosulfonate on the hydration of various cement constituents by x-ray diffraction and observed that sucrose accelerated the reaction between gypsum and C_3A ; but lignosulfonate had little, if any, acceleration effect. Lignosulfonate inhibited the release of $Ca(OH)_2$ from C_3S and also suppressed the release of alkali into the liquid phase. The alkali is supposed to react chemically with the retarder to destroy its hydration inhibiting effect. They concluded:

"Materials that cause retardation of set, such as sucrose or lignosulfonates, can also produce a large initial acceleration of the hydration reactions. This acceleration may be caused by inhibition of lime release by the silicates phases or by increased reactivity of the C_3A with gypsum, resulting from the very high sorption of the additive in the C_3A surface. The early acceleration and high sorption can be avoided by delayed addition of the retarder; the retarding effect is then markedly increased."

Kalousek et al. (20) analyzed extracts from various clinkers at 7 minutes and 2 hr after mixing and observed that sucrose was the only added material (the others being gypsum, $CaCl_2$, calcium acetate, fluosilicic acid, TDA, tannic acid, and triethanolamine) that increased the basicity of the extract. This was observed not only by increased extraction of alkali, but also, to a greater extent, by almost complete conversion of dissolved sulfate to insoluble products. Thus sucrose accelerated the early hydration involving the alumina-bearing constituents of the clinkers.

Tamas (21) assumed that retarders would behave in the opposite manner to calcium chloride and suggested that retarders formed an adsorbed layer on the grain of cement silicates, causing de-activation of the reaction between the silicate phase and water. He also suggested the possibility of the formation of insoluble compounds between retarders and the aluminates in cement.

An interesting result was shown by Ramachandran (22). He examined the adsorption and desorption isotherms of calcium lignosulfonate from both aqueous and non-aqueous solutions on C_3S , hydrated C_3S , and lime. It was the hydrated C_3S , but not C_3S , that was responsible for a perceptible amount of adsorption of calcium lignosulfonate from the aqueous solution. Because the adsorption was irreversible, he suggested surface complex formation (chemisorption) involving the silicate surface, calcium lignosulfonate, and water.

It appears that silicate phases in portland cement can not be neglected in considering the interaction between retarders and cement and, therefore, the retardation mechanism in cement paste. Long ago, Steinour (23) said, "Indeed, in cements with good contents of gypsum in which setting is due to hydration of tricalcium silicate, it is logical to assume that in order to obtain further retardation it is the reaction of the silicate that must be slowed up."

From the review of literature in this section, the following summary of information is meaningful:

1. C_3A , C_4AF , hydrated C_3S , and, possibly, hydrated C_3A adsorb retarders from solution.
2. Retarders that have chemically different structures act differently in their effects on cement hydration.
3. Not only the aluminate phase but also the silicate phase in cement plays a significant role in the setting process.
4. Retarders are more effective when they are added to cement of low C_3A and low alkali content.

Effective Molecular Structure of Retarder and Retardation Mechanism

Hansen (24) found that most of the organic compounds that retarded the hydration of oil well cements had a common structural feature of the H-C-OH group. He later suggested that large anions of retarders could react by ionic bonding with the calcium ions in the surface of cement minerals and that OH groups react by hydrogen bonding with oxide ions of the minerals. Thus the organic compounds block the contact of cement granules with water molecules and so inhibit hydration (11).

Steinour (25) showed that retarders characterized by undissociated OH groups retarded β - C_2S hydration. Because these retarders are effective at small concentrations, and

because the OH groups can form hydrogen bonds, he assumed that they retard the hydration of cement by an adsorption mechanism (23, 26).

Taplin (27) added a large number of inorganic and organic chemicals to cement paste to find out the effective molecular structure of retarders. He found that the group HO-C-C=O was usually present in organic substances that retard the hydration of portland cement, and that the effective molecules usually contain at least two oxygen atoms each bound to a single but different carbon atom in such a way that the oxygen atoms can approach each other. However, there were some exceptions. He also showed that location and arrangement of OH groups in molecules changed the retardation power widely. His proposed retardation mechanism is the adsorption of these chemicals (i) on the surface of clinker minerals so as to protect them from attack by water and (ii) on the surface of a coherent coating of hydration products so as to prevent transport of materials to or from the clinker surface.

Danielson (28) made cement pastes with thirteen different organic calcium salts and measured the setting time of the pastes. He concluded that the retarding capacities of the salts were related to the characteristics of the added molecule in a way that suggests a confirmation of the hypothesis proposed by Hansen and many other workers, namely that retardation is due to adsorption of the molecules on cement grains.

Previte (29) measured the end point of the dormant period in the course of hydration of cement paste by isothermal calorimetry and showed that saccharides of larger molecular weight generally were more powerful as retarders when they were added on an equimolar basis. However, the rate of alkaline degradation was another factor affecting the set retardation effectiveness. He concluded that the effect of alkalinity in the aqueous phase of hydrating cement reduces the set retardation efficiency of alkaline-degradable saccharides.

Bruere (30) examined why the dissaccharide α , α -trehalose had been found to possess only weak retarding ability, while all other sugars studied were powerful set-retarders. Only α , α -trehalose failed to produce any trace of cuprous oxide in boiling Fehling's solution at all alkali concentrations used, whereas all the other sugars produced significant amounts of cuprous oxide in the test solution. He postulated that the latter could hydrolyse significantly in the highly alkaline conditions in cement paste to produce reducing sugars that in turn could be converted to saccharinic acids containing the HO-C-C=O group, and thus he supported Taplin's theory even in the case of saccharides.

But according to Daugherty and Kawalewski (13), α , α -trehalose is a powerful retarder for the hydration of C_3A , and it retards the hydration to the same extent as

sucrose. They also found that OH groups tend to retard the hydration of C_3A and carbonyl ($C=O$) groups tend to accelerate the hydration of C_3A , but the α -hydroxyl carbonyl ($HO-C-C=O$) group itself did not appear to be important.

Koide (31) stated that carboxyl ($COOH$) group has always retarded the hydration of CA (the principal component of high-alumina cement). The effect was especially marked when the group was contained in a chelating compound (example; EDTA) that produce sexadendates of high stability.

In a review, Young (32) postulated that organic retarders adsorb on calcium hydroxide nuclei in cement pastes and poison their future growth. Retardation is the result of this delayed formation of calcium hydroxide. He further explained that higher levels of calcium hydroxide supersaturation are required to overcome the effects of the retarders.

Summarizing this section, most workers believe that the retardation of cement hydration is a result of the adsorption of the retarder molecules on the surface of cement grains or hydration products. The adsorption may be by hydrogen bonding. However not much is known of the effect of the molecular structure of the retarders. The different results for α , α -trehalose found by different workers indicate that the behavior of retarders in cement paste may not necessarily be the same as that in pure compound systems.

Drying Shrinkage of Paste, Mortar, and Concrete
as Affected by Retarders

When retarders (or water reducing admixtures) are added to concrete, the subsequent drying shrinkage is generally thought to increase (4, 33). On the other hand, Wallace and Ore (3) examined the test results reported by many field laboratories and concluded that these admixtures neither increase nor decrease the shrinkage of concrete. This uncertainty of the effect of retarders on the shrinkage of concrete arises from the many complicated factors that affect shrinkage (34, 35). Tremper and Spellman (4) demonstrated that the cumulative effects of some factors on shrinkage could be expressed by the product, not the sum, of individual effects. Hence, the true effect of retarders on the shrinkage of concrete has to be examined carefully so that indirect influences are avoided. However, only a few papers have been published concerning the shrinkage behavior as affected by retarders.

Danielson (28) observed that the shrinkage of cement paste in an atmosphere of 60% R.H. was, in general, increased by the admixtures studied. The increase was considerable when benzonate and salicylate, which were the only aromatic salts examined, were added.

Tremper (36) dried mortar specimens that were 4 days old for 4 days in an atmosphere of 50% R.H. At low SO_3 contents of the cement, the admixtures (lignosulfonate and hydroxylated carboxylic acid) increased drying

significantly. At higher SO_3 contents the trend was reversed, and in most cases the drying shrinkage decreased relative to that of mortars containing no admixture. Thus he suggested that the optimum gypsum content in cement should be increased to minimize the shrinkage when admixtures are added.

In cement paste, gypsum reacts with C_3A and forms the high-sulfate form of calcium sulfoaluminate hydrate (ettringite) in early stages of hydration. This reaction is known to be expansive. According to Lerch (37), for cements of low alkali content, those of high C_3A content require larger additions of gypsum to give minimum subsequent shrinkage than do those of low C_3A content. For cements of the same C_3A content, those of high alkali content require larger addition of gypsum than do those of low alkali content. Therefore, the observation by Tremper could be related to some modified rate of hydration of the cement caused by the retarders.

Another conceivable cause could be changes in the structure of the hydration products. Young (6) observed that no new hydrate was formed in C_3A hydration by the addition of calcium lignosulfonate, but a modification of the crystal habit of the usual hydrates took place; acicular structures were formed instead of hexagonal plates of C_2AH_8 and C_4AH_{13} . When gypsum was present, the formation of high sulfoaluminate was not affected by the

admixture. However, the final hydration products (low sulfoaluminate, C_2AH_8 , and C_4AH_{13}) were changed from their usual hexagonal plate form.

Danielson (28) examined the properties of cement paste affected by organic admixtures at an age of 28 days. The amount of combined water and the total heat of hydration were not altered significantly by the admixtures. The compressive strength was also either unaffected or somewhat lowered. The reduction in Young's modulus was unexpectedly small compared with the reduction in compressive strength for all the pastes to which dibasic salts were added. He attributed this result to a modified structure of hydration products.

On the other hand, Seligmann and Greening (8) showed that sucrose and lignosulfonate did not affect the nature of the hydration reaction of cement; only the rate was influenced. Prior and Adams (1) mentioned that differential thermal analysis studies of hydrated cement at the ages of 7 and 28 days showed no significant change in the identity or proportion of the hydration products of cement with the addition of lignosulfonates.

By means of a scanning electron microscope, Schwieter, Ludwig, and Sieler (38) examined the morphology of the hydration products of cement pastes at the ages of 1, 7, 14, and 28 days. There was no difference observed among them regardless of the addition of different kinds of

retarders. These workers also confirmed, by means of x-ray diffraction, that retarders changed only the rate of hydration of the cement.

CHAPTER III - MATERIALS

Admixtures

A total of sixty-five chemicals were tested in the setting time experiments to examine the effects of the molecular structure of the retarders. They included a variety of organic chemicals - many aliphatic compounds, aromatic compounds, chelating agents, dyes and others. About one half were organic acids. Their names, chemical formulae, and producer's names are listed in Table 1.

The three commercially available proprietary retarders L, A, and S were used throughout the work. Each represents one of the three main categories of organic retarders, i.e., calcium (also, sodium or ammonium) lignosulfonates, hydroxycarboxylic acids, and carbohydrates, respectively. Since the commercial retarders were supplied in solution form, their solids content was determined by oven-drying in the usual way. Density and amount of solid content of each commercial retarder are shown in Table 2. It should be noted that concentrations of all retarders are, hereafter, discussed in terms of weight of the solid component per unit weight of cement in the mixture.

Table 1 - List of Chemicals

Name	Chemical Formula	Company
Malonic Acid	$\text{CO}_2\text{HCH}_2\text{CO}_2\text{H}$	Eastman
Succinic Acid	$\text{CO}_2\text{H}(\text{CH}_2)_2\text{CO}_2\text{H}$	Allied Chem.
Glutaric Acid	$\text{CO}_2\text{H}(\text{CH}_2)_3\text{CO}_2\text{H}$	Eastman
Adipic Acid	$\text{CO}_2\text{H}(\text{CH}_2)_4\text{CO}_2\text{H}$	Fisher
Glycolic Acid	$\text{CO}_2\text{HCH}_2\text{OH}$	Fisher
Glycine	$\text{CO}_2\text{HCH}_2\text{NH}_2$	M.C. & B.
Mercaptoacetic Acid (liq.)	$\text{CO}_2\text{HCH}_2\text{SH}$	M.C. & B.
Monochloroacetic Acid	$\text{CO}_2\text{HCH}_2\text{Cl}$	Mallinckrodt
Glyoxylic Acid (Hydrate)	$\text{CO}_2\text{HCHO} \cdot x\text{H}_2\text{O}$	Aldrich
Pyruvic Acid (liq.)	$\text{CO}_2\text{HCOCH}_3$	M.C. & B.
Lactic Acid (85% liq.)	$\text{CO}_2\text{HCHOHCH}_3$	Mallinckrodt
α -Hydroxy-N-Butyric Acid (liq.)	$\text{CO}_2\text{HCHOHCH}_2\text{CH}_3$	K & K
Ketomalonic Acid (Disodium)	$\text{CO}_2\text{NaCOCO}_2\text{Na}$	Aldrich
Tartronic Acid	$\text{CO}_2\text{HCHOHCO}_2\text{H}$	Aldrich
(-) Malic Acid	$\text{CO}_2\text{HCHOHCH}_2\text{CO}_2\text{H}$	J. T. Baker

Table 1, cont.

Name	Chemical Formula	Company
(d) - Tartaric Acid	$\text{CO}_2\text{H}(\text{CHOH})_2\text{CO}_2\text{H}$	Mallinckrodt
Dihydroxymaleic Acid	$\text{CO}_2\text{H}(\text{COH})_2\text{CO}_2\text{H}$	Aldrich
Dihydroxytartaric Acid	$\text{CO}_2\text{H}(\text{C}(\text{OH})_2)_2\text{CO}_2\text{H}$	Aldrich
3-Hydroxypropionic Acid	$\text{CO}_2\text{HCH}_2\text{CH}_2\text{OH}$	Aldrich
Mucic Acid	$\text{CO}_2\text{H}(\text{CHOH})_4\text{CO}_2\text{H}$	Aldrich
Gluconic Acid (50% liq.)	$\text{CO}_2\text{H}(\text{CHOH})_4\text{CH}_2\text{OH}$	Eastman
2-Ketoglutaric Acid	$\text{CO}_2\text{H}(\text{CH}_2)_2\text{COCO}_2\text{H}$	Aldrich
1,2,3-Propanetricarboxylic Acid	$\text{CO}_2\text{HCH}_2\text{CH}(\text{CO}_2\text{H})\text{CH}_2\text{CO}_2\text{H}$	Eastman
Citric Acid	$\text{CO}_2\text{HCH}_2\text{C}(\text{OH})(\text{CO}_2\text{H})\text{CH}_2\text{CO}_2\text{H}$	Mallinckrodt
Crotonic Acid	$\text{CH}_3\text{CH}:\text{CHCO}_2\text{H}$	M.C. & B.
Acetaldol (liq.)	$\text{CH}_3\text{CHOHCH}_2\text{CHO}$	Aldrich
Methyl Glycolate (liq.)	$\text{CH}_3\text{OCOCH}_2\text{OH}$	K & K
α -Hydroxyacetamide	$\text{NH}_2\text{COCH}_2\text{OH}$	K & K
1,3-Dihydroxy-2-Propanone	$\text{CH}_2\text{OHCOCH}_2\text{OH}$	Eastman
Glycerin (liq.)	$\text{CH}_2\text{OHCHOHCH}_2\text{OH}$	Fisher
3-Hydroxy-2-Butanone (liq.)	$\text{CH}_3\text{COCHOHCH}_3$	Eastman

Table 1, cont.

Name	Chemical Formula	Company
N-Methylpropionamide (liq.)	$\text{CH}_3\text{CH}_2\text{CONHCH}_3$	Eastman
Ethyl Acetoacetate (liq.)	$\text{CH}_3\text{COCH}_2\text{COOCH}_2\text{CH}_3$	M.C. & B.
Allyl Alcohol (liq.)	$\text{CH}_2=\text{CHCH}_2\text{OH}$	Fisher
2-Butene-1,4-Diol (liq.)	$\text{CH}_3\text{OHCH}:\text{CHCH}_2\text{OH}$	Aldrich
Chloral Hydrate	$\text{C}(\text{Cl})_3\text{CH}(\text{OH})_2$	Aldrich
Pentaerythritol	$\text{C}(\text{CH}_2\text{OH})_4$	Eastman
2,4 - Pentanedione (liq.)	$\text{CH}_3\text{COCH}_2\text{COCH}_3$	M.C. & B.
Sucrose	$\text{C}_6\text{H}_{11}\text{O}_5-\text{O}-\text{C}_6\text{H}_{11}\text{O}_5$	Baker
Resorcinol	$\text{m}-\text{C}_6\text{H}_4(\text{OH})_2$	Eastman
Catechol	$\text{o}-\text{C}_6\text{H}_4(\text{OH})_2$	M.C. & B.
Hydroquinone	$\text{p}-\text{C}_6\text{H}_4(\text{OH})_2$	Fisher
m-Nitrophenol	$\text{m}-\text{NO}_2\text{C}_6\text{H}_4\text{OH}$	Baker
o-Nitrophenol	$\text{o}-\text{NO}_2\text{C}_6\text{H}_4\text{OH}$	M.C. & B.
p-Nitrophenol	$\text{p}-\text{NO}_2\text{C}_6\text{H}_4\text{OH}$	M.C. & B.
m-Hydroxybenzoic Acid	$\text{m}-\text{HO}\cdot\text{C}_6\text{H}_4\text{CO}_2\text{H}$	Aldrich

Table 1, cont.

Name	Chemical Formula	Company
Salicylic Acid	$\text{o-HO} \cdot \text{C}_6\text{H}_4\text{CO}_2\text{H}$	Baker
p-Hydroxybenzoic Acid	$\text{p-HO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$	Eastman
Benzoic Acid	$\text{C}_6\text{H}_5\text{CO}_2\text{H}$	Baker
Benzyl Alcohol (liq.)	$\text{C}_6\text{H}_5\text{CH}_2\text{OH}$	Baker
DL-Mandelic Acid	$\text{C}_6\text{H}_5\text{CH(OH)CO}_2\text{H}$	Aldrich
o-Hydroxyacetophenone (liq.)	$\text{HOC}_6\text{H}_4\text{COCH}_3$	Aldrich
Picric Acid	$2,4,6-(\text{NO}_2)_3 \cdot \text{C}_6\text{H}_2\text{OH}$	Baker
Pyrogallol	$1,2,3-(\text{HO})_3 \cdot \text{C}_6\text{H}_3$	Fischer
Phloroglucinol	$1,3,5-(\text{HO})_3 \cdot \text{C}_6\text{H}_3 \cdot 2\text{H}_2\text{O}$	M.C. & B.
Galic Acid	$3,4,5-(\text{HO})_3 \cdot \text{C}_6\text{H}_2\text{CO}_2\text{H}$	Eastman
2,4,6-Trihydroxybenzoic Acid (Monohydrate)	$2,4,6-(\text{HO})_3 \cdot \text{C}_6\text{H}_2\text{CO}_2\text{H} \cdot \text{H}_2\text{O}$	Aldrich
EDTA (Disodium)	*	Mallinckrodt
Nitritotriacetic Acid (Disodium)	$\text{HOCOCH}_2\text{N}(\text{CH}_2\text{COONa})_2$	Eastman

* $(\text{CH}_2\text{CO}_2\text{H}) (\text{CH}_2\text{CO}_2\text{Na})\text{N}(\text{CH}_2)_2\text{N}(\text{CH}_2\text{CO}_2\text{Na}) (\text{CH}_2\text{CO}_2\text{H})$

Table 1, cont.

Name	Chemical Formula	Company
Dye 27195	-----	---
Dye 25380	-----	---
Dye 24410	-----	---
Dye 42755	-----	---
Eriochrome Black T	-----	Fisher
Calcium Lignosulfonate	-----	----

Table 2 - List of Commercial Retarders.

Retarders		Density (g/cc)	Residue* (g/cc)
Name	Chemical Classification		
L	Calcium Lignosulfonate	1.147	0.370
A	Hydroxycarboxylic Acid	1.152	0.413
S	Carbohydrate (Sugar)	1.175	0.376

*Weight of residue was obtained by oven-drying retarder at 110°C.

In the shrinkage experiments, five reagent grade chemicals that had been found to be retarders were selected and used along with the three commercial retarders. The pure compounds were glycolic acid, citric acid, 3-hydroxy-2-butanone, sucrose, and hydroquinone. Reagent grade calcium chloride was also included to investigate the effects of an accelerator.

Cement

The cement used was an ASTM Type I, Lab. No. 319, the properties of which are shown in Table 3. Since a great number of setting time measurements on mortar specimens were conducted for more than a year, some cements had changed slightly during storage, and it was found that the cements thus partially hydrated and possibly carbonated had slower setting properties. This difficulty was

Table 3 - Composition and Properties of Lab Cement No. 319.

<u>Chemical Analysis</u>		<u>Compound Composition</u>	
	(%)		(%)
SiO ₂	21.64	C ₃ S	56.03
Al ₂ O ₃	5.29	C ₂ S	19.86
Fe ₂ O ₃	2.19	C ₃ A	10.31
CaO	65.36	C ₄ AF	6.66
MgO	0.92	CaSO ₄	4.08
SO ₃	2.40	Total	96.94
Na ₂ O	0.08		
K ₂ O	0.41		
Loss on Ignition	1.80		
Total	100.18		
Free Lime	1.08		
Insoluble Residue	0.25		
<u>Physical Tests</u>			
Normal Consistency (ASTM C187)		24.5 (%)	
Expansion (ASTM C151)		0.136 (%)	
Setting Time; Gilmore (ASTM C266):			
Initial		2:55	
Final		4:15	
Fineness; Blaine (ASTM C204)		3870 (cm ² /g)	
Paste False Set (ASTM C451)		93.5 (%)	
Air Entrained (ASTM C185)		8.3 (%)	
Compressive Strength (ASTM C109):			
1 day		1550 (psi)	
3 day		3130 (psi)	
7 day		4600 (psi)	
28 day		6450 (psi)	
Tensile Strength (ASTM C190):			
1 day		205 (psi)	
3 day		345 (psi)	
7 day		430 (psi)	
28 day		520 (psi)	

overcome by running a blank test on a plain mortar as a control once a month or whenever cement was taken from a new sack.

For shrinkage measurements of paste samples and for some chemical experiments only one sack of cement was selected and stored in sealed glass bottles.

Sand

The sand used in the preparation of mortar specimens for setting time determinations had a specific gravity of 2.63, 1.33% absorption, and a fineness modulus of 2.26 and 2.45 for the two lots used. These were masonry mortar sands with more than 99% passing the No. 8 sieve, because it was thought that large sand particles might result in erroneous penetration values when a small needle was used. In use, these sands were oven-dried for 24 hr at 110°C and stored in a temperature controlled room at 21°C.

Water

In the setting-time experiments, tap water was used to prepare the mortar specimens. The water was put in a polyethylene bottle and stored in the same temperature controlled room.

Deionized or distilled water was used for all of the other experiments in this paper. These include chemical analyses and preparation of cement paste specimens.

CHAPTER IV - EXPERIMENTAL WORK

A - Setting Time Measurements

General Remarks

The setting times were determined by the Proctor penetration method, ASTM Designation: C403. This method involves obtaining a mortar sample by wet-screening concrete to remove the coarse aggregate and is time-consuming and requires large amounts of materials. It has been shown (39) that the setting time of concrete can be determined from that of a directly-mixed mortar if the mortar is made with the same water-cement ratio, sand-cement ratio, and materials as the concrete. Therefore, it was decided to measure the penetration resistance of directly-mixed mortar as the method of evaluating chemicals as retarders. Mix proportions corresponding to those of a practical concrete were chosen for the mortar. Initial setting time and final setting time are, according to C403, defined as the elapsed times to reach penetration resistances of 500 psi and 4000 psi, respectively. This definition has been used in this work.

All materials were stored in a temperature-controlled room at 21°C, and all operations were conducted in the same room.

Apparatus

Container

One-gallon cardboard containers, with a diameter of 6.75 in., were used to contain the mortar; this represents a slight modification of Method C403.

Since the containers are not as rigid as metal containers, it was suspected that the value of penetration resistance might vary with the location that was probed in the surface of the sample. However preliminary experiments showed that the differences among the measurements were negligibly small if the test was conducted within a circle located 1 inch in from the side of the container.

Penetration Resistance Apparatus

A hand-loaded Proctor apparatus was used. The spring was calibrated by means of a platform scale. The calibration curve is shown in Figure 1.

Mixer

A model A200 Hobart Mixer was used. The slow speed was determined to revolve the paddle at a rate of 94 rpm, with a planetary motion of 47 rpm. The medium speed revolved the paddle at a rate of 180 rpm, with a planetary motion of 90 rpm.

Total capacity of the mixing bowl was 20 liters, and an optimum mix volume was felt to be about 7 liters.

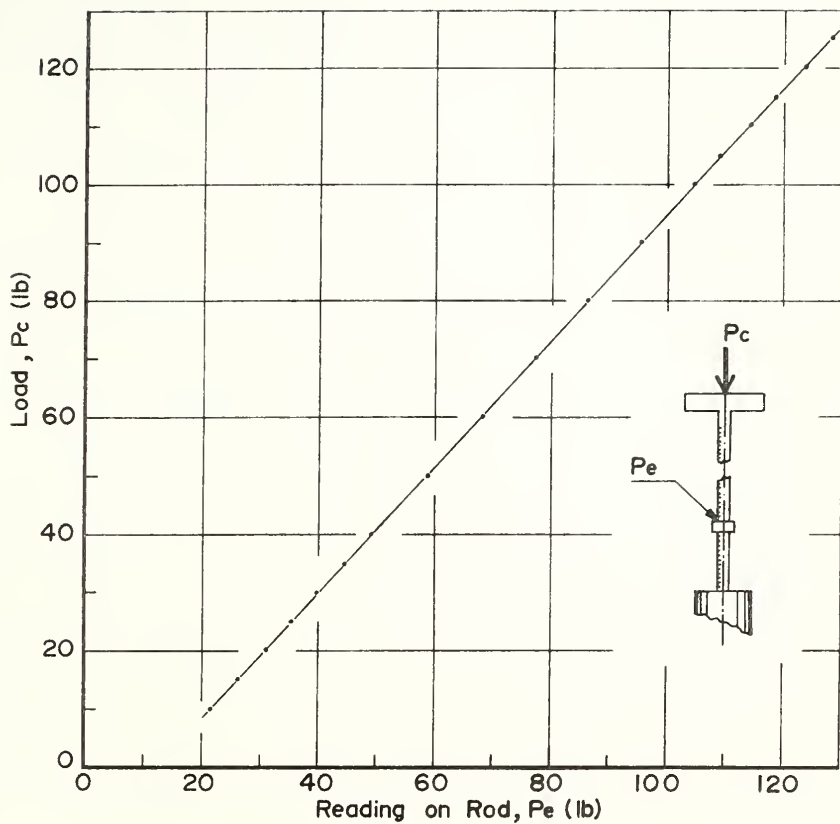


Figure 1 - Calibration Curve for Proctor Penetrometer
(ASTM C403)

Preparation of Mortar Specimens

Mixing Proportions and Size of Batch

Constant mix proportions were maintained throughout the experiments. The water to cement ratio was 0.50, and the sand to cement ratio was 2.75, by weight. These are typical of ratios used in concrete mixtures. The mortar thus proportioned was plastic and workable. Since the sand was oven-dried, the actual water to cement ratio of the mortars was a little lower than 0.50.

In preliminary experiments it was found that three values of penetration resistance from three samples had a range of less than 5% of the average value, in every case. It was therefore determined to prepare a mix of 6 2/3 liters, and two test samples were prepared from this batch.

The reagent chemicals used as admixtures were added at a concentration of 0.1% of the cement by weight in most cases, although sometimes others were used to determine the influence of concentration. For the three commercial retarders, various concentrations were tested depending on each manufacturer's suggested dosage.

Mixing Procedures

The admixture was added to the mixing water and stirred until dissolved completely. Some relatively insoluble substances required heating for dissolution. The solution thus prepared was placed in the mixing bowl, and the

cement was added. They were mixed at the slow speed for 30 seconds. The mixing operation was interrupted for about 5 sec during which time the sand was added. Mixing was resumed at slow speed for 30 sec and, then for 1 min at medium speed. Then the mixing was stopped for 1 minute. During this period, all the mortar on the blade of the mixer and the wall of the bowl was scraped down with a spatula. The mixture was again mixed at medium speed for an additional 1 minute. Mortars thus prepared had flow values of 110 to 140%, according to ASTM Method C87, depending on the admixture used.

Casting and Storage of Specimens

The mixed mortar was placed in the two containers and was compacted by rodding 25 times. The surface of the specimen was then approximately leveled with a trowel, and the side of the container was tapped lightly with the tamping rod. The distance between the finished surface of the mortar sample and the top edge of the container was approximately 1 inch. The sample and container were covered with a damp cloth, and the lid was placed on.

Penetration Test Procedure

ASTM C403 was followed exactly. Six to seven penetration resistance determinations were made on most specimens. Some samples did not reach the final setting time within 24 hr; in such instances the test was stopped after 24 hr,

mainly because there was no location left for further penetration measurements on the surface of the sample.

A needle was selected for each penetration of such a size that the load on it was between 40 and 90 lb, a range in which the most reliable values were obtained.

B - Measurement of Shrinkage of Cement Pastes

General Considerations

Because of the impermeability of cement paste and its consequent slowness of drying, it was desired to use small specimens for the shrinkage experiments to minimize both the time to reach drying equilibrium and the moisture (and therefore, strain) gradients within the specimen. Homogeneity and reproducibility are required for such small specimens.

A possibly troublesome effect with small specimens is carbonation of the cement paste by reaction with atmospheric CO_2 , which can induce more shrinkage than drying (35). Another consideration is that cement paste continues to hydrate for a comparatively long period of time. This continued hydration changes the structure of the paste and, therefore, affects the shrinkage behavior. Since many retarders modify the early hydration of cement, this effect of continued hydration is of significant importance in this study. With these considerations in mind, the following apparatus and techniques were employed.

Apparatus

Mold for Cement Paste Specimens

A special mold was made of Teflon so that the paste specimens could be demolded without using any parting medium, such as oil. Thus the surfaces of the specimens were free from any contamination, so that uniform drying could be attained. The mold is shown in Figure 2 together with a cement paste specimen.

A total of ten specimens could be made at one casting. The size of the specimen was $1/5 \times 1/5 \times 4$ inch. A small hole was made through the centers of the opposite end blocks to accommodate the gauge studs for the length change measurements.

Some specimens had to be demolded at about 7 to 10 hr after casting. In these cases a thin polyethylene sheet was placed between the teflon mold and the specimen. In spite of this effort, about half of the specimens were broken on demolding.

Gauge Studs and Length Comparator

Gauge studs were needed to measure the length changes of the cement paste bars. The studs used were the ends clipped from empty ball-point pen refills made of stainless steel. These were inserted in the end blocks with the ball-portion outward so that after casting about 3 mm of the shaft was embedded in the paste specimen. The ball

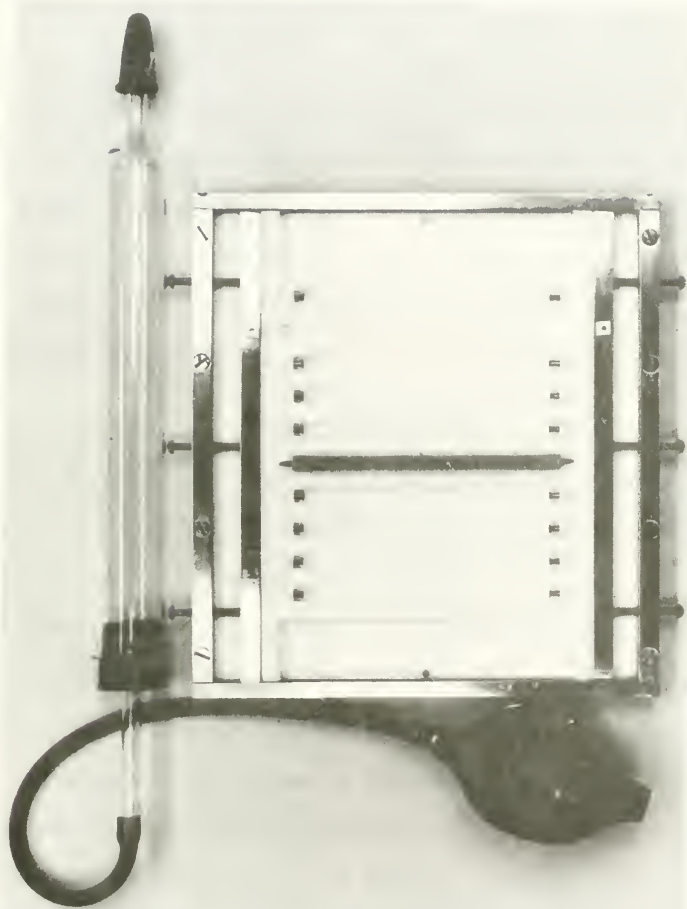


Figure 2 - Mold for Cement Paste Specimens, Cement Paste Sample, and Paste Caster

portions proved to be ideal as gauge studs and showed no deformation, to 0.0001 in., within themselves.

The length comparator is shown in Figure 3. All elements except the base plate were stainless steel. The dial gauge provided a maximum stroke of 0.3 in., and the smallest subdivision was 0.0001 inch. Since the length of the cement paste bars was 4 in., a length change of 0.0025% could be determined. A standard bar was also made of stainless steel to compensate the effects of temperature fluctuation on the gauge distance of the apparatus. It was enclosed in a rubber tube to eliminate heat transfer from the hand to the bar during handling.

Mixing Apparatus

A vacuum mixing container was made from stainless steel tubing. A stainless steel plate was welded to one end of the tube, and a circular slit was made on the other end to accommodate an O-ring. The O-ring provided the seal between the container and the lid. The lid was attached to the container by means of four clamping screws. On the side of the container was inserted a vacuum-tight stainless-steel needle valve, through which the container was evacuated and through which a measured amount of water was introduced into the container. The inside dimension of the container was 3 x 4 inch. The size was so determined that a paste made from 100g of cement could be mixed efficiently and

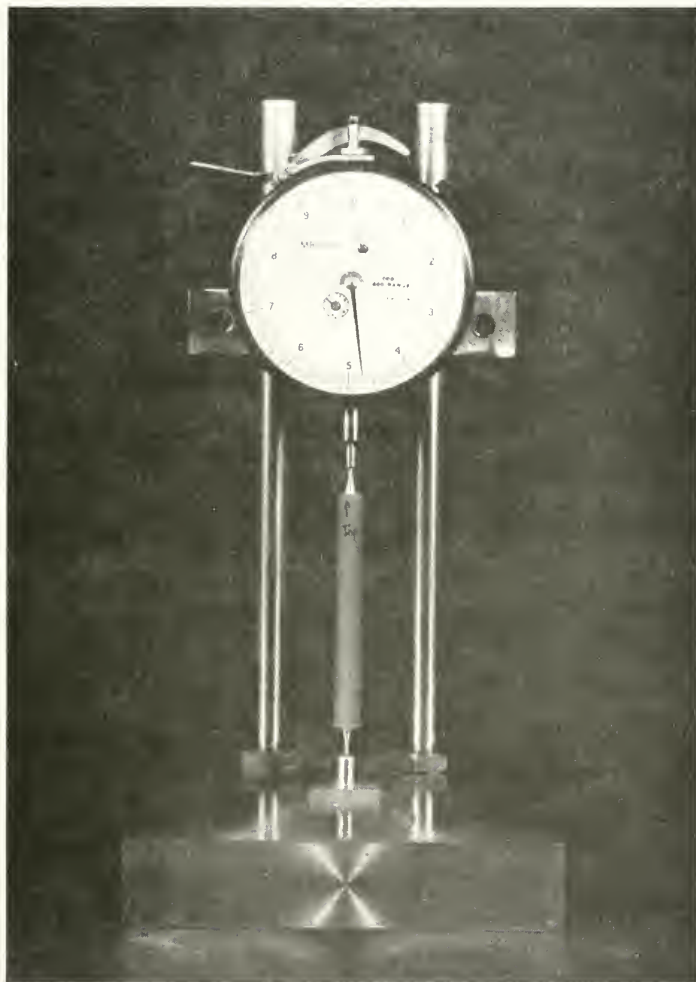


Figure 3 - Length Comparator

uniformly by a shaking action. The shaking action was provided by a Red Devil paint shaker.

Preparation of Cement Paste Specimens

Mixing Proportion and Concentration of Retarders

It was desirable to use a water-cement ratio as close as possible to that normally used in concrete mixtures. A ratio of 0.40, however, was found to be the maximum allowable for a cement paste to be mixed and cast without experiencing a significant amount of bleeding; this ratio was employed throughout.

The three commercial retarders (L, A, and S) and five pure chemicals (citric acid, glycolic acid, hydroquinone, 3-hydroxy-2-butanone, and sucrose), each representing a certain group of retarders, were used. Their concentrations were determined on the basis of the results of setting time experiments on mortars. The relationship between concentration of retarder and initial setting time of the mortar containing it was plotted and the concentration that gave 50% of additional retardation to a reference mortar containing no admixture was established from the curve. The values obtained are given in Table 4. Additionally calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$), an accelerator of set, was used at a concentration of 1% of the cement by weight.

Table 4 - Concentration of Retarders Added to Cement Pastes.

Retarder		Concentration (percent of cement)
Commercial Retarders	L	0.260
	A	0.065
	S	0.100
Pure Chemicals	Citric Acid	0.050 (0.076) *
	Glycolic Acid	0.135
	Hydroquinone	0.080
	3-Hydroxy-2- Butanone	0.400
	Sucrose	0.050

* This is the concentration which gives 100% of additional retardation to a reference mortar. Others give 50% of additional retardation.

Mixing, Casting, and Curing of Cement Paste Specimens

The cement was placed in the mixing container. The lid was attached and the four clamping screws were tightened. The container was evacuated on an aspirator for 10 to 15 minutes. During this time, 80 ml of deionized water were poured into a graduated separatory funnel and the required amount of admixture, if necessary, was dissolved in it. The evacuated mixing container was closed with the needle valve and then was removed from the aspirator. The solution was then drawn from the funnel into the container by opening the valve. The valve was closed again when the required amount of the solution, 40 ml in most cases, had been introduced into the container. The apparatus is shown in Figure 4.

The container was then placed on the shaker and shaken for 5 minutes. This method yielded an extremely uniform paste mixture that contained no entrained air.

After the shaking the paste was removed from the container and placed in a "cake-decorator" type of apparatus made of a pyrex glass tube with a squeezable ball attached to one end (Figure 2). The cement paste was cast in the mold from the paste caster. First the bottom of one gauge stud was filled; and the upper part next. The other end was then filled in the same way, and the rest of the mold was filled continuously from one end to the other. The paste was cast slightly above the surface of the mold, and

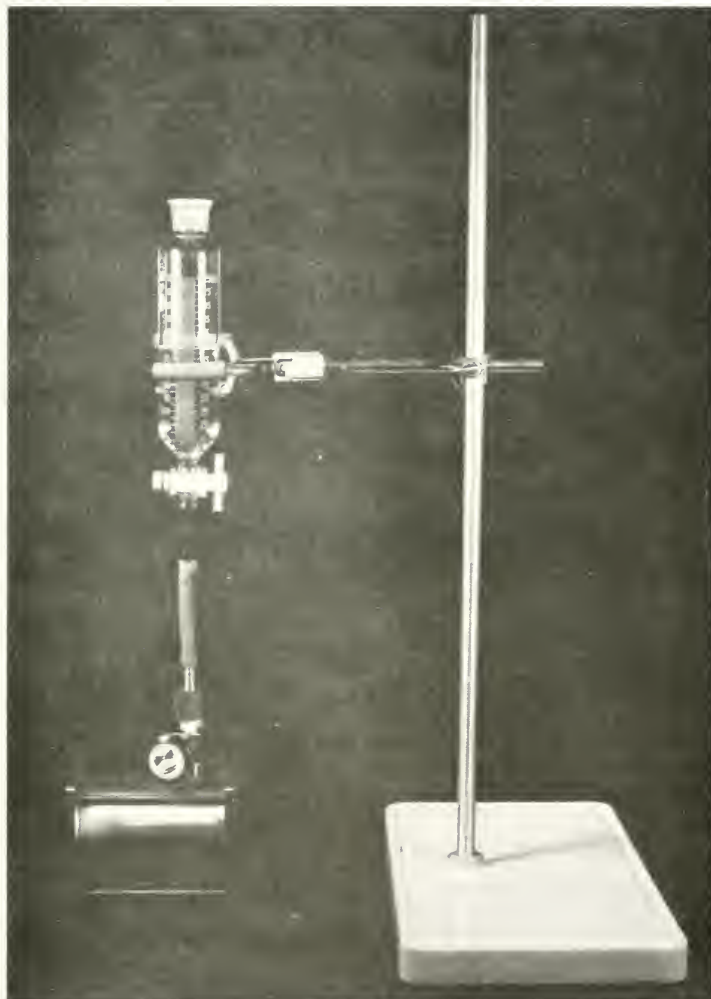


Figure 4 - Apparatus for Drawing Mixing Solution from Funnel into Mixing Container

was later sliced off at the time of demolding to eliminate any effects of either bleeding or carbonation. The mold was then placed on a vibrating table (paper jogger) and was vibrated briefly. This general technique produced uniform specimens with a minimum amount of bleeding. Finally, the specimens in the mold were covered with damp cloths arranged so that they did not come in direct contact.

The specimens that were tested at an age of 4 days or later were demolded at 2 days. The other specimens were demolded at 7 to 22 hr after the mixing depending on the kind of admixture added or the desired age of specimens. The specimens were then immersed in closed containers in a saturated calcium hydroxide solution.

Measurements of Length and Weight, Method of Drying

At the desired age the specimens were measured for length change, weight change, and degree of hydration. The specimen was taken from the curing bottle and was placed in the length comparator in the standard manner. The length was recorded in the wet state. After the measurement, the sample was returned in the storage bottle.

Shortly thereafter, the sample was again taken from the bottle, the studs and the body of the paste bar were wiped with tissue paper, and the weight was measured rapidly on an analytical balance, to the nearest 0.1 mg.

The specimen was then dried in a vacuum oven controlled at 105 to 110°C, which was continuously evacuated on a vacuum pump. This was a severe drying condition and unrealistic for concrete in the field. It was used to shorten the time of drying, to eliminate carbonation, and to minimize the effects of continuing hydration of the cement. At the end of the drying time the specimen was taken out of the oven and was cooled to room temperature in a desiccator over anhydrous magnesium perchlorate.

The specimen was then weighed. The length change was measured with the Ames-dial comparator. This sequence was based on the observation that the weight of the dried sample was very sensitive to exposure to air, whereas the length was not especially so. Some very young specimens had warped longitudinally. However, deflection at mid-length (due to warping) was less than 0.5 mm for most specimens. Calculation showed that errors caused by such a warping were less than an experimental error of length measurement, and no correction was made. Only four specimens warped more than 0.5 mm at the center; they were corrected for lengths, using the curve shown in Appendix A. Shrinkage was calculated with respect to the water-saturated length.

After all measurements, the specimen was broken into three approximately equal lengths. The middle third was used immediately for the determination of non-evaporable

water, and the other two portions were stored in a vial out of contact with air.

Some relatively mature paste specimens were tested after drying in air of 50% relative humidity at room temperature. These specimens were placed in a desiccator over a saturated salt solution of $\text{Mg}(\text{NO}_3)_2$. A chemical sorbent for CO_2 was also placed in the desiccator, which was then evacuated. Changes of length and weight were measured at various times in the same manner described above.

C - Determination of Degree of Hydration of Cement Pastes

Loss on Ignition Test

The degree of hydration of the cement in the paste was determined by measuring the amount of chemically combined, or non-evaporable, water. Direct determinations were made by the Penfield method (40), which has certain drawbacks. It was decided to conduct a loss on ignition test and to calculate the amount of non-evaporable water from the result. The derivation of the equation used is shown in the next section.

The loss on ignition was determined in the usual way, using approximately 1g samples of the crushed, oven-dry paste in platinum crucibles. The heating was in a muffle furnace to constant weight at about 1050°C.

Derivation of Equations for Determining Non-Evaporable Water and Evaporable Water

Loss on ignition has sometimes been considered a measure of the degree of hydration of cement paste. But this idea is misleading. Even an unhydrated cement has a loss on ignition of around 1%, because the loss on ignition includes not only non-evaporable water, but also carbon dioxide from carbonated compounds.

In hardened cement paste, most bulk water is evaporable at relatively low temperature. However, some water molecules are sorbed on cement gel with a differentiating degree of bond strength. As a result the distinction between chemically-combined (non-evaporable) water and physically sorbed (evaporable) water is possible only on an empirical basis. In this study, therefore, they were defined as follows:

"Evaporable Water": Water lost from a sample during vacuum oven drying at 105-110°C for 24 hours.

"Non-Evaporable Water": Water remaining in a sample during vacuum oven drying of 24 hr at 110°C and lost on drying at about 1050°C.

Assumptions

In the derivation of these equations it was assumed that chemically combined water or carbon dioxide (due to inadvertent exposure to atmosphere) in the "dry" cement are not lost on vacuum oven drying to 110°C and that any further carbonation during mixing, curing, and drying of

the paste is negligible. In any case the pastes prepared for this study had carbonated only slightly.

Notation

Schematic diagrams for "dry" cement and for cement paste are shown in Figure 5. The notations are:

W _e	: weight of evaporable water in cement paste
W _n *	: weight of chemically combined water <u>after</u> mixing
W _n	: total weight of non-evaporable water in cement paste
W _c	: total weight of cement
W _{ce}	: weight loss of cement when dried in the vacuum oven for 24 hr at 110°C
W _{clw}	: weight of chemically combined water in cement <u>before</u> mixing
W _{clc}	: weight of chemically combined carbon dioxide in cement <u>before</u> mixing
W _{cl}	: (W _{clw} + W _{clc})
W _{ch}	: weight of cement hydrated in cement paste
W _{cu}	: weight of cement unhydrated in cement paste
W _{ci}	: ignited weight of cement at 1050°C (=W _{ch} + W _{cu})
W _l	: total weight loss on ignition of cement <u>before</u> mixing
W _{li}	: weight loss on ignition of cement paste <u>after</u> being dried in the vacuum oven for 24 hr at 110°C
W _{ss}	: weight of water saturated surface dry cement paste
W _{od}	: weight of the same sample after dried in the vacuum oven for 24 hr at 110°C

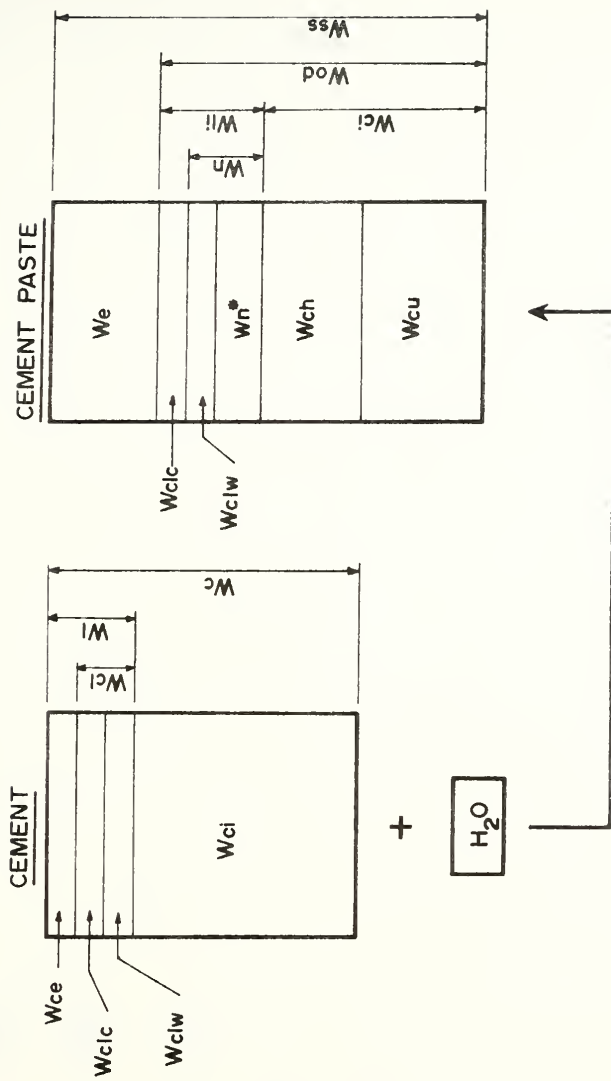


Figure 5 - Schematic Diagrams of Cement and Cement Paste

Derivation of Equations

Immediately obtainable relations are,

$$Wc = Wci + Wcl + Wce = Wci + Wl \text{ ----- (1)}$$

$$Wcl = Wclc + Wclw \text{ ----- (2)}$$

$$Wss = Wci + Wcl + Wn^* + We \text{ ----- (3)}$$

$$Wod = Wci + Wcl + Wn^* \text{ ----- (4)}$$

$$Wli = Wn^* + Wcl \text{ ----- (5)}$$

From eq. (5),

$$\frac{Wli}{Wci} = \frac{Wn^* + Wcl}{Wci} \therefore \frac{Wn^*}{Wci} = \frac{Wli}{Wci} - \frac{Wcl}{Wci} \text{ ----- (6)}$$

Combining eqs. (3) and (4), and dividing by Wci,

$$\begin{aligned} \frac{We}{Wci} &= \frac{Wss - Wod}{Wci} = \frac{Wss - Wod}{Wod} \times \frac{Wod}{Wci} \\ &= \left(\frac{Wss}{Wod} - 1 \right) \times \left(1 + \frac{Wcl}{Wci} + \frac{Wn^*}{Wci} \right) \text{ ----- (7)} \end{aligned}$$

Substituting eq. (6) into eq. (7),

$$\frac{We}{Wci} = \left(\frac{Wss}{Wod} - 1 \right) \left(1 + \frac{Wli}{Wci} \right) \text{ ----- (8)}$$

$$\begin{aligned} \frac{We}{Wc} &= \frac{We}{Wci} \times \frac{Wci}{Wc} = \frac{We}{Wci} \times \frac{(Wc - Wl)}{Wc} \\ &= \left(\frac{Wss}{Wod} - 1 \right) \left(1 + \frac{Wli}{Wci} \right) \left(1 - \frac{Wl}{Wc} \right) \text{ ---- (9)} \end{aligned}$$

Dividing both terms of eq. (2) by Wci,

$$\begin{aligned} \frac{Wcl}{Wci} &= \frac{Wclc}{Wci} + \frac{Wclw}{Wci} \\ \therefore \frac{Wclw}{Wci} &= \frac{Wcl}{Wci} - \frac{Wclc}{Wci} \\ &= \frac{Wcl}{Wci} - \frac{Wclc}{Wc} \times \frac{Wc}{Wci} \text{ ----- (10)} \end{aligned}$$

Since $W_n = W_n^* + W_{clw}$,

$$\frac{W_n}{W_{ci}} = \frac{W_n^* + W_{clw}}{W_{ci}} \quad \text{-----} \quad (11)$$

Substituting eqs. (6) and (10) into eq. (11),

$$\frac{W_n}{W_{ci}} = \frac{W_{li}}{W_{ci}} - \frac{W_{clc}}{W_c} \times \frac{W_c}{W_{ci}} = \frac{W_{li}}{W_{ci}} - \frac{W_{clc}}{W_c} \left(1 + \frac{W_l}{W_{ci}}\right) \quad \text{--} \quad (12)$$

$$\frac{W_n}{W_c} = \frac{W_n}{W_{ci}} \times \frac{W_{ci}}{W_c} = \frac{W_n}{W_{ci}} \left(1 - \frac{W_l}{W_c}\right) \quad \text{-----} \quad (13)$$

It should be noted that W_{ci} includes also the part of cement which has been carbonated before mixing with water and, therefore, is not available for hydration. Calculation, however, showed that the true W_n/W_{ci} and W_c/W_{ci} did not differ by more than 1% from the calculated values from eqs. (8) and (12). Because the experimental error of loss on ignition test amounts to the calculative error, no further consideration was made.

Reduction of Data

The following equations were derived and used to reduce loss on ignition data in this study.

$$\frac{W_n}{W_{ci}} = \frac{W_{li}}{W_{ci}} - \frac{W_{clc}}{W_c} \left(1 + \frac{W_l}{W_{ci}}\right) \quad \text{-----} \quad (14)$$

$$\frac{W_n}{W_c} = \frac{W_n}{W_{ci}} \left(1 - \frac{W_l}{W_c}\right) \quad \text{-----} \quad (15)$$

$$\frac{W_e}{W_c} = \left(\frac{W_{ss}}{W_{od}} - 1\right) \left(1 + \frac{W_{li}}{W_{ci}}\right) \left(1 - \frac{W_l}{W_c}\right) \quad \text{-----} \quad (16)$$

W_{li}/W_{ci} can be determined directly from the loss on ignition test, as can W_l/W_{ci} and W_l/W_c . W_{cl}/W_c was determined by a common method (41). The value of W_l/W_c varied from 0.0196 to 0.0203 during the shrinkage study. $(W_{cl}/W_c) \times (1 + W_l/W_{ci})$ ranged only from 0.01091 to 0.01092. W_{ss} and W_{od} were obtained from the specimens used for the length change measurements. In calculating W_{ss} and W_{od} , the weight of the gauge studs was, of course, subtracted from the total weight of the specimen. Degree of hydration was expressed by dividing W_n/W_{ci} of a sample by that of fully hydrated cement paste.

D - Surface Area Measurements of Cement Pastes

General Remarks

Water vapor and nitrogen are the two gases commonly used for measuring the surface area of a solid by the adsorption method. These gases, however, give surface areas of a different order of magnitude for cement paste. Typical BET surface areas of a mature cement paste by water vapor and by nitrogen sorption are $200 \text{ m}^2/\text{g}$ and $20 \text{ m}^2/\text{g}$, respectively. Because the surface area is one of the important factors of a model of cement paste structure there has been a critical controversy between some workers concerning the value of surface area and the method of measuring it (42, 43, 44, 45). This controversy is yet

unresolved. In this study, since only relative values were needed, the water vapor adsorption value was chosen.

Apparatus and Procedures of Measurement

Four glass desiccators were prepared with solutions of glycerin and deionized water to control the vapor pressure of water. The relative humidities ranged from 10 to 32 per cent. The concentration of glycerin in the solution, and hence the relative humidity, was determined by the measurement of the refractive index of the solution. Approximately 1 liter of each solution was placed in the desiccator and continuously stirred with a magnetic stirrer.

The cement paste samples, which had been vacuum-oven dried for the shrinkage measurements, were ground in a mortar and pestle so that most passed a No. 60 sieve. The powdered samples were placed on watch glasses and were re-dried in the vacuum oven for an additional hour at 110°C. After drying, the samples were placed in weighed weighing bottles. Lids were placed while the samples were still hot. The bottles were cooled to room temperature in a desiccator and weighed. The weight of the sample was about 1g.

The bottles were placed in the desiccator of the lowest humidity and their lids were removed. The desiccator was closed and evacuated on a vacuum pump. Adsorption was allowed to continue for 48 hours. Then the desiccator was opened, and the bottles were covered with the lids. They were weighed and replaced in the desiccator of the next

lowest humidity, and the process was repeated. The refractive index of the solution was tested after the bottles were taken out of the desiccator, and the temperature was recorded.

The adsorption isotherms were interpreted in the usual way by the BET Theory (46, 47). The rectified form of the equation was used and the data were analyzed by least squares; the calculation was made by a computer. Specific surface area was expressed on the basis of ignited weight of the cement paste sample.

E - Scanning Electron Microscope Observation

General Procedures

The model JSM-U3 scanning electron microscope, Japan Electron Optics Laboratory Co. Ltd., was used for the observation of the samples.

At the desired age, the sample was oven-dried at 110°C and mounted on a brass sample holder. The sample was stored in a desiccator over anhydrous magnesium perchlorate until the mounting glue dried. It was necessary to coat the sample, usually only with carbon, to get a clear image. The sample was then placed in the microscope and the image of the sample was first observed on a TV screen at a relatively low magnification. Various locations of the sample were viewed in detail by changing the magnification,

and a desired representative area was determined on the screen. Then the image was switched from the TV screen to the probe screen of the microscope and examined further in detail. Finally, photomicrographs were taken with a Polaroid camera. The scanning speed at this time was slowed down to 50 seconds.

CHAPTER V - RESULTS

Infrared Spectra of Commercial Retarders

The three commercial retarders were representative of the three main categories in current use. To identify them more precisely, a small amount of each was oven-dried at 110°C, and KBr pellets were made and infrared spectra obtained in the usual way with a Beckman DK-10 spectrophotometer. Figure 6 shows the results. The interpretations of individual absorption bands follow the assignments given by Halstead and Chaiken (48). That marked L is a lignosulfonate retarder, A is a hydroxycarboxylic acid retarder, and S is a modified sugar or carbohydrate, probably with some other materials in it that remain unidentified.

Non-Evaporable Water Content of Fully Hydrated Cement Paste

The non-evaporable water content of fully hydrated cement was needed to calculate the degree of hydration of the cement paste samples. The value was determined by hydrating the cement as follows: 45 g of the cement and 450 ml of distilled water were placed in a clean 16-ounce glass bottle and a lid was placed on it with a teflon sheet as a lid-liner. The bottle was rotated continuously on a

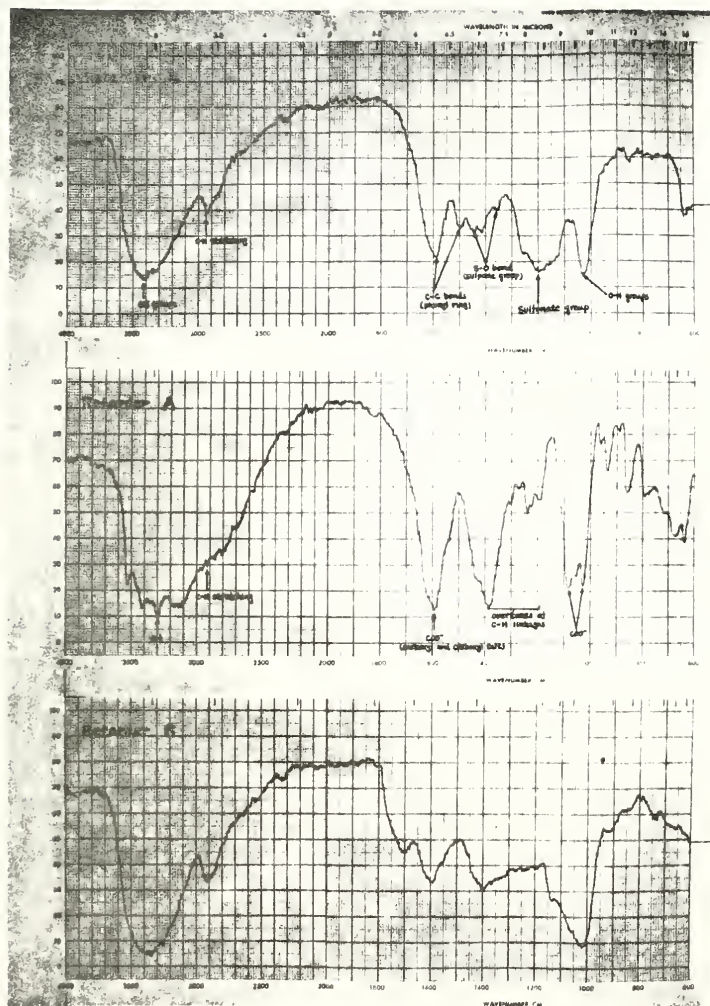


Figure 6 - Infrared Spectra of Commercial Retarders

roller mill for 10 days. The mixing was then changed to magnetic stirring until the time of test. At this time the sample was vacuum filtered on paper, and the residue was placed in the vacuum oven at 105 to 110°C. Loss on ignition of the oven-dry sample was then determined by furnace drying at 1050°C.

The results of the determination conducted at hydration times of 4 and 10 weeks are shown in Table 5. Most of the cement had hydrated in 4 weeks; only a little further hydration was observed from 4 weeks to 10 weeks. Hence, the values at the age of 10 weeks were employed as those of the fully hydrated cement in this work.

Table 5 - Non-Evaporable Water Content of Bottle-Hydrated Cement (W/C = 10).

Age (weeks)	Loss on Ignition W _{li} /W _{ci} (%)	Non-Evaporable Water W _n /W _{ci} (%)
4	19.81	18.72
10	20.59	19.50

Result of Setting Time Experiments

Commercial Retarders

Figures 7, 8, and 9 show the results of setting time experiments for the three commercial retarders when they were used at different concentrations, expressed as weight percent of the retarder-solids based on the cement. In these figures, values of penetration resistance are plotted against elapsed time after initial contact of the cement with mixing water (plus admixture). The general expectation that the higher the concentration of retarder, the longer the setting time, is apparent. However, it is noteworthy that the retarders A (hydroxycarboxylic acid) and S (carbohydrate) tend to accelerate the initial hydration of cement when they were added at the highest concentration whereas the retarder L (lignosulfonate) retards all stages of the hydration evenly up to 4000 psi even at higher concentration.

In order to compare the effects of concentration of retarders at different penetration levels, Figures 10, 11, and 12 were made from the same results. It is observed that relative retardation of the mortars is smaller at higher penetration resistances. This is an important and necessary property for properly retarded concrete. Another interesting point is that the increases in setting time at the penetration resistance levels of 500, 1000, and 4000 psi are in close agreement and the retardation at 500 psi

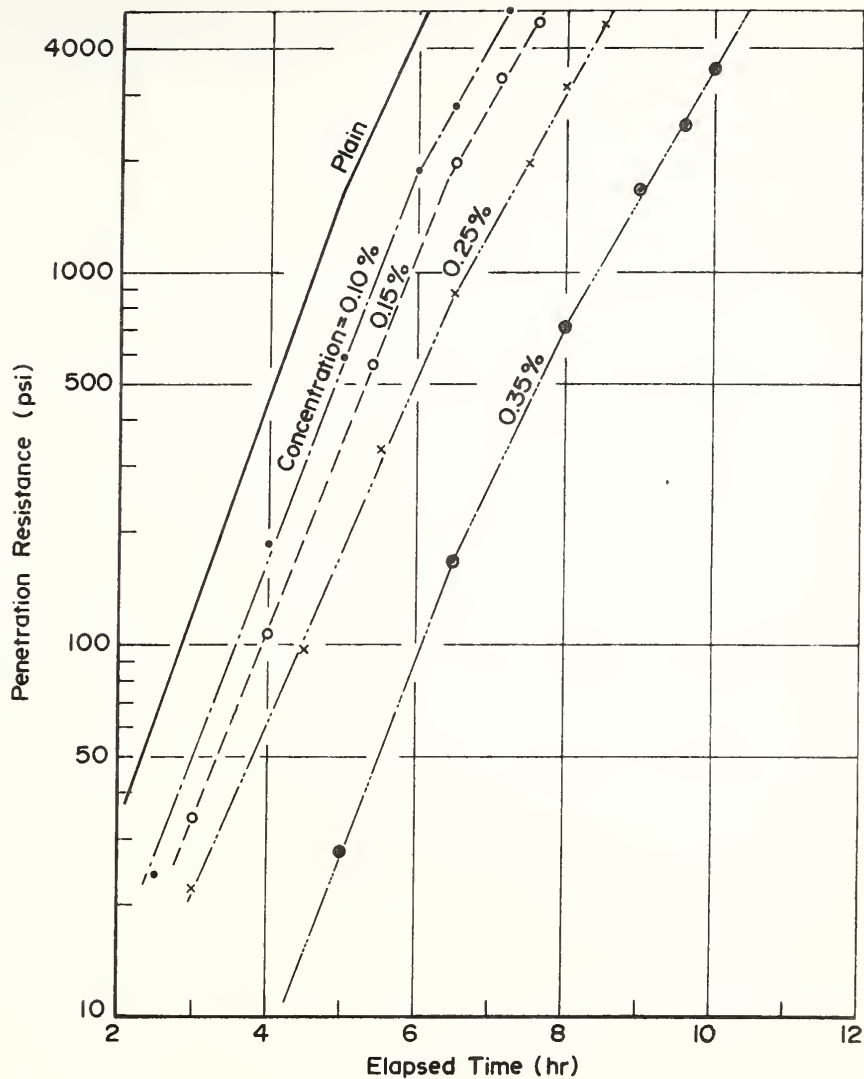


Figure 7 - Penetration Resistance vs Elapsed Time for Mortar with Retarder L

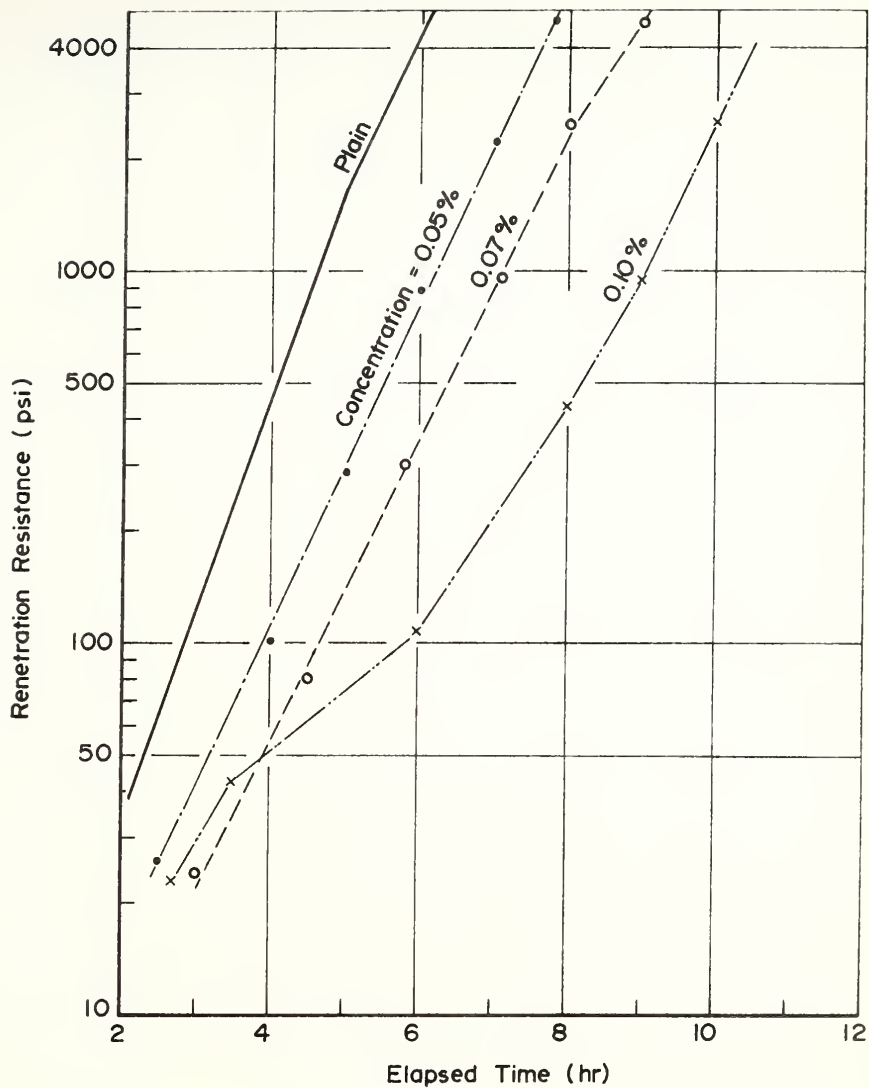


Figure 8 - Penetration Resistance vs Elapsed Time for Mortar with Retarder A

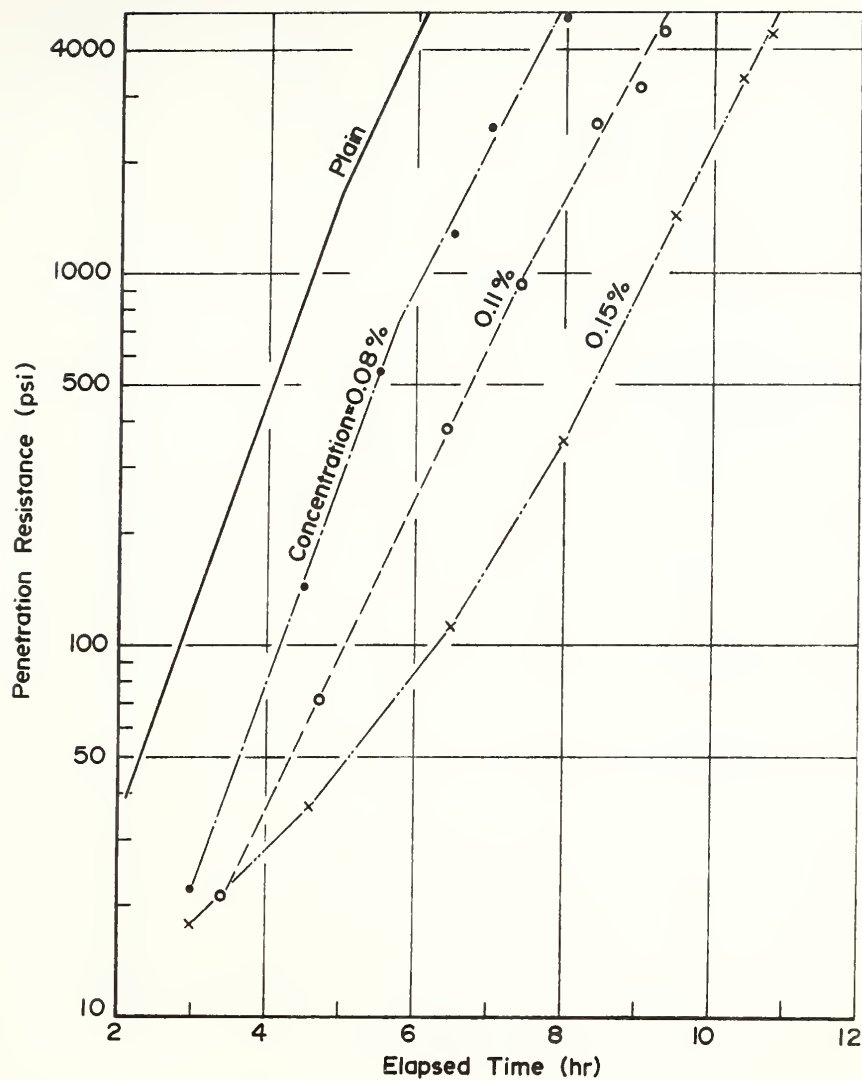


Figure 9 - Penetration Resistance vs Elapsed Time for Mortar with Retarder S

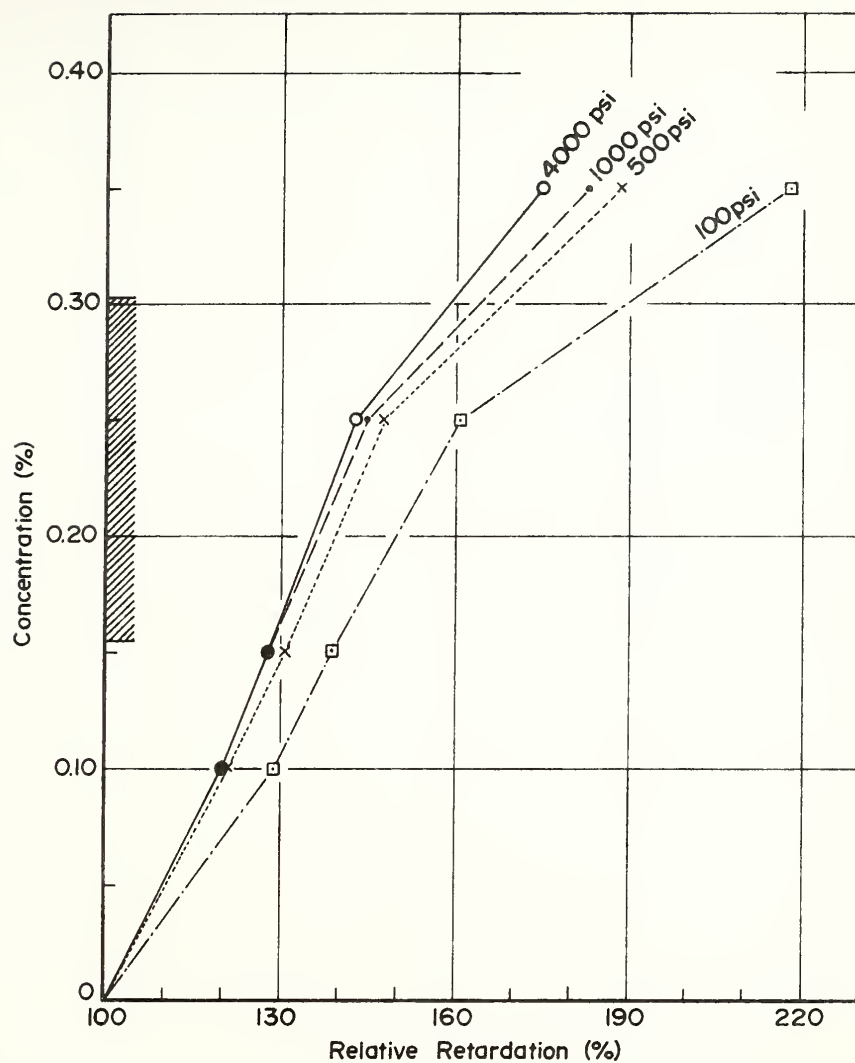


Figure 10 - Effect of Concentration of Retarder L on Setting Time of Mortar

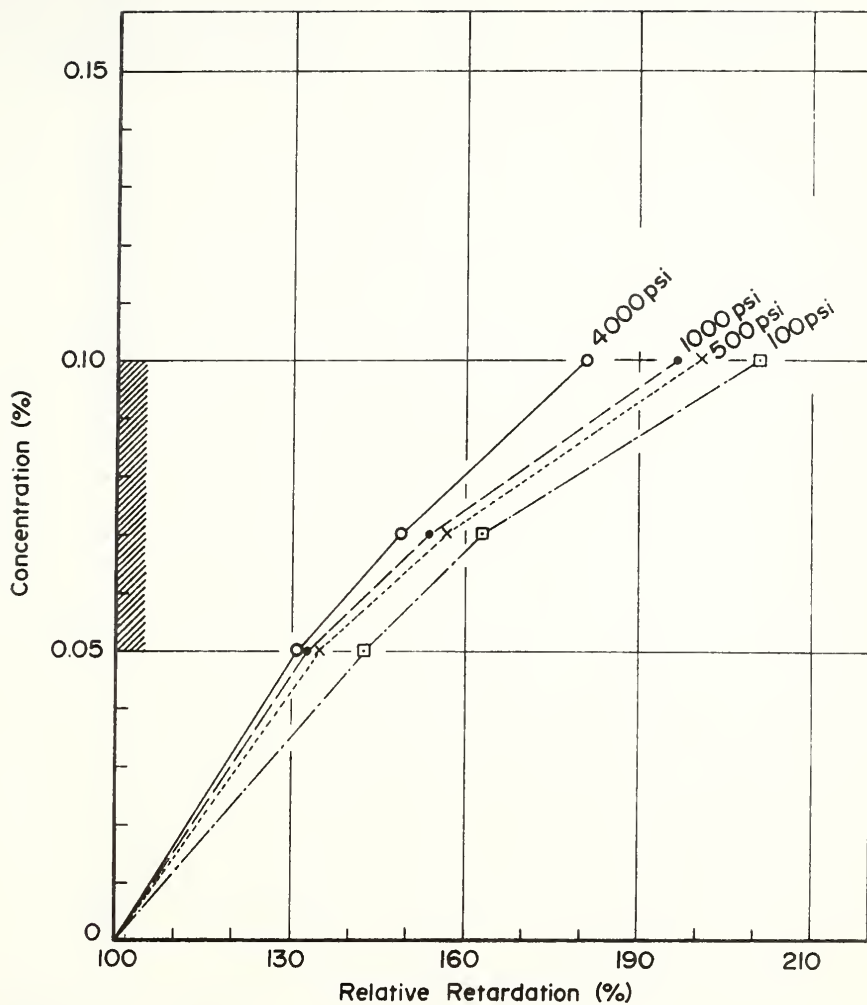


Figure 11 - Effect of Concentration of Retarder A on Setting Time of Mortar

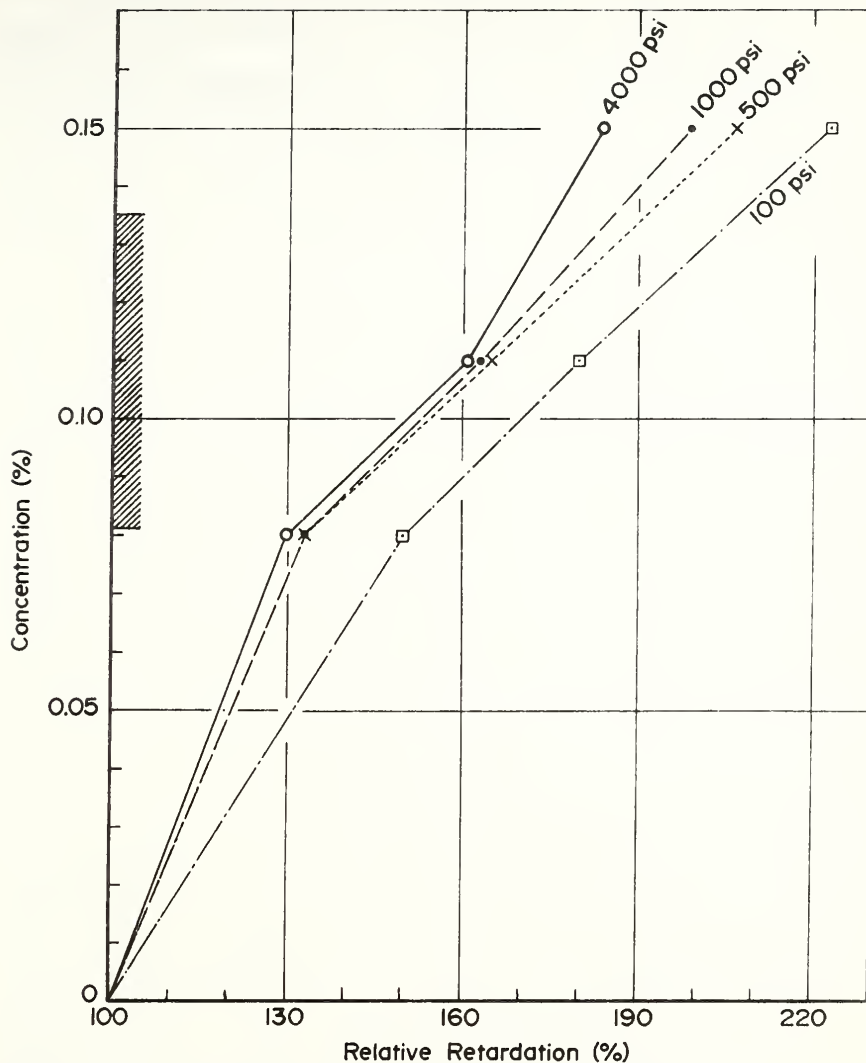


Figure 12 - Effect of Concentration of Retarder S on Setting Time of Mortar

level appears to be a mean retardation in the resistance range of 100 to 4000 psi. Since initial setting time corresponds approximately to the last time when revibration of concrete can be made, the result would indicate that initial setting time is a practical and convenient standard point for evaluating retarders.

Manufacturer's suggested dosages are also shown in each figure by a shaded range. These dosages produce increases in setting time of roughly 30 to 90% for all the retarders. The resulting range of retardation is typical of that of concrete (49). This result implicitly affirms the adequacy of the penetration resistance test as conducted on mortar specimens in this work. In the same figures, it should be noted that the lignosulfonate retarder (L) required more than twice as much dosage as the others (A and S) did to obtain a certain amount of retardation.

Pure Chemicals

Table 6 summarizes the initial setting times of mortar specimens incorporating many chemicals at a concentration of 0.1% of the cement by weight. For some of the chemicals that were found to be a weak or ineffective retarder at a concentration of 0.1%, other results of tests at a concentration of 0.5% are also shown. T500 is defined as the initial setting time of each sample relative to that of a control sample, and was obtained as follows: A relationship between elapsed time and penetration resistance

Table 6 - Summary of Relative Initial Setting Time of Mortars When Pure Chemicals Were Added

Chemical	Concentration of Chemical			
	0.1%		0.5%	
	T500	T500/T50	T500	T500/T50
Malonic Acid	102	0.93	145	0.90
Succinic Acid	110	1.05	137	1.12
Glutaric Acid	110	1.00	100	0.97
Adipic Acid	101	0.97	-	-
Glycolic Acid	128	0.94	*	2.45**
Glycine	100	1.00	96	0.97
Mercaptoacetic Acid	113	1.00	128	0.91
Monochloroacetic Acid	-	-	108	1.02
Glyoxylic Acid (Hydrate)	127	1.04	-	-
Pyruvic Acid	207	1.06	-	-
Lactic Acid	102	1.00	118	0.96
α -Hydroxy-N-Butyric Acid	100	1.02	-	-
Ketomalonic Acid (Disodium)	154	1.01	-	-
Tartronic Acid	278	2.32	-	-
(-) Malic Acid	198	1.01	-	-

* Retardation was too large to determine in the limit of the experiment.

** T100/T50 instead of T500/T50.

Table 6, cont.

Chemical	Concentration of Chemical			
	0.1%			0.5%
	T500	T500/T50	T500	T500/T50
(d)-Tartaric Acid	254	1.27	-	-
Dihydroxymaleic Acid	141	1.05	-	-
Dihydroxytartaric Acid	166	1.19	-	-
3-Hydroxypropionic Acid	102	1.02	-	-
Mucic Acid	257	1.24	-	-
Gluconic Acid	>300	>2.00	-	-
2-Ketoglutaric Acid	292	1.38	-	-
1,2,3-Propanetricarboxylic Acid	139	0.99	-	-
Citric Acid	286	1.43	-	-
Crotonic Acid	101	0.97	-	-
Acetaldol	103	0.97	93	0.93
Methyl Glycolate	113	1.11	315	1.20
α -Hydroxyacetamide	112	1.04	*	1.22**
1,3-Dihydroxy-2-propanone	125	1.04	97	2.06
Glycerine	-	-	92	0.96
3-Hydroxy-2-Butanone	107	0.94	173	0.91
N-Methylpropionamide	109	0.96	-	-
Ethyl Acetoacetate	107	0.88	177	1.01

Table 6, cont.

Chemical	Concentration of Chemical			
	0.1%			0.5%
	T500	T500/T50	T500	T500/T50
Allyl Alcohol	100	0.96	-	-
2-Butene-1,4-Diol	100	1.00	102	0.94
Chloral Hydrate	-	-	104	0.99
Pentaerythritol	102	1.04	-	-
2,4-Pentanedione	108	0.92	-	-
Sucrose	>300	>1.50	-	-
Resorcinol	98	0.92	-	-
Catechol	127	1.14	-	-
Hydroquinone	198	0.92	-	-
m-Nitrophenol	107	0.98	-	-
o-Nitrophenol	109	1.00	-	-
p-Nitrophenol	102	1.01	-	-
m-Hydroxybenzoic Acid	103	1.00	-	-
Salicylic Acid	122	0.96	-	-
p-Hydroxybenzoic Acid	102	1.04	-	-
Benzoic Acid	103	0.98	-	-
Benzyl Alcohol	101	0.97	-	-
DL-Mandelic Acid	107	1.07	-	-

Table 6, cont.

Chemical	Concentration of Chemical			
	0.1%		0.5%	
	T500	T500/T50	T500	T500/T50
o-Hydroxyacetophenone	108	1.05	-	-
Picric Acid	117	1.04	112	1.05
Pyrogallol	239	1.17	-	-
Phloroglucinol	131	1.07	-	-
Gallic Acid	257	1.08	-	-
2,4,6-Trihydroxybenzoic Acid (Monohydrate)	217	1.30	-	-
EDTA (Disodium)	139	1.02	184	1.11
Nitritotriacetic Acid (Disodium)	134	0.93	-	-
Dye 27195 (282)	100	1.03	-	-
Dye 25380 (353)	96	1.04	-	-
Dye 24410 (518)	110	0.97	-	-
Dye 42755 (707)	102	0.98	-	-
Eriochrome Black T	103	0.98	-	-
Calcium Lignosulfonate	118	0.96	-	-

was drawn for each sample in the same way as was done for the commercial retarders, and an initial setting time was determined. This time was then expressed in terms of a percentage of that of an appropriate control sample without admixture. In the same way, T50, T100, and T4000, which are relative setting times at the penetration resistance of 50, 100, and 4000 psi, respectively, were determined. They are to be found in Appendix B. A tendency, similar to that observed with the commercial retarders, was noted - namely the relative setting time at 500 psi, T500, is about the same value as the corresponding T100 and T4000. T50 is different from the other relative setting times for some chemicals. If T50 is smaller than the others, it indicates that the chemical accelerated, relatively speaking, the very early hydration of cement. The ratio $T500/T50$ was used for this indication in Table 6, i.e., the larger the ratio the more the reactions were relatively accelerated. Strong retarders such as tartronic acid, d-tartaric acid, mucic acid, gluconic acid, 2-ketoglutaric acid, citric acid, sucrose, and 2,4,6-trihydroxybenzoic acid have large values of $T500/T50$.

Again, calcium lignosulfonate is not a strong retarder. Glycolic acid, methyl glycolate and α -hydroxyacetamide are strong retarders at higher concentrations. Only 1,3-dihydroxy-2-propanone showed an unusual setting when it was added at the rate of 0.5%. It accelerated early

hydration of the cement to reach a penetration resistance of 200 psi in 2 hr, but extremely retarded the later hydration. This behavior was similar to that observed in the hydration of a Type I cement clinker without any gypsum addition (Figure 13).

Figures 14 and 15 show the effects of concentration of admixture on the relative initial setting time of mortar specimens. It is seen that strong retarders can delay the setting of mortars almost indefinitely even at a relatively low concentration while some other chemicals accelerate the setting when added at higher concentration.

The results seem to divide themselves into two groups. In Figure 14, whatever the magnitude of the retardation, additional increments of concentration produced an increasingly larger relative retardation, i.e., the curves are concave downward. In Figure 15, on the other hand the opposite is true; the instances showed less additional effect at higher concentrations. Indeed, sometimes the effect was reversed.

Effects of Retarders on the Drying Shrinkage of Cement Paste at Various Stages of Hydration

Figures 16 and Figure 17 show, respectively, the shrinkage of the cement paste bars as affected by the addition of commercial retarders and selected pure chemicals when the pastes were dried in a vacuum oven at 105 to 110°C for 24 hours. The shrinkage values were plotted

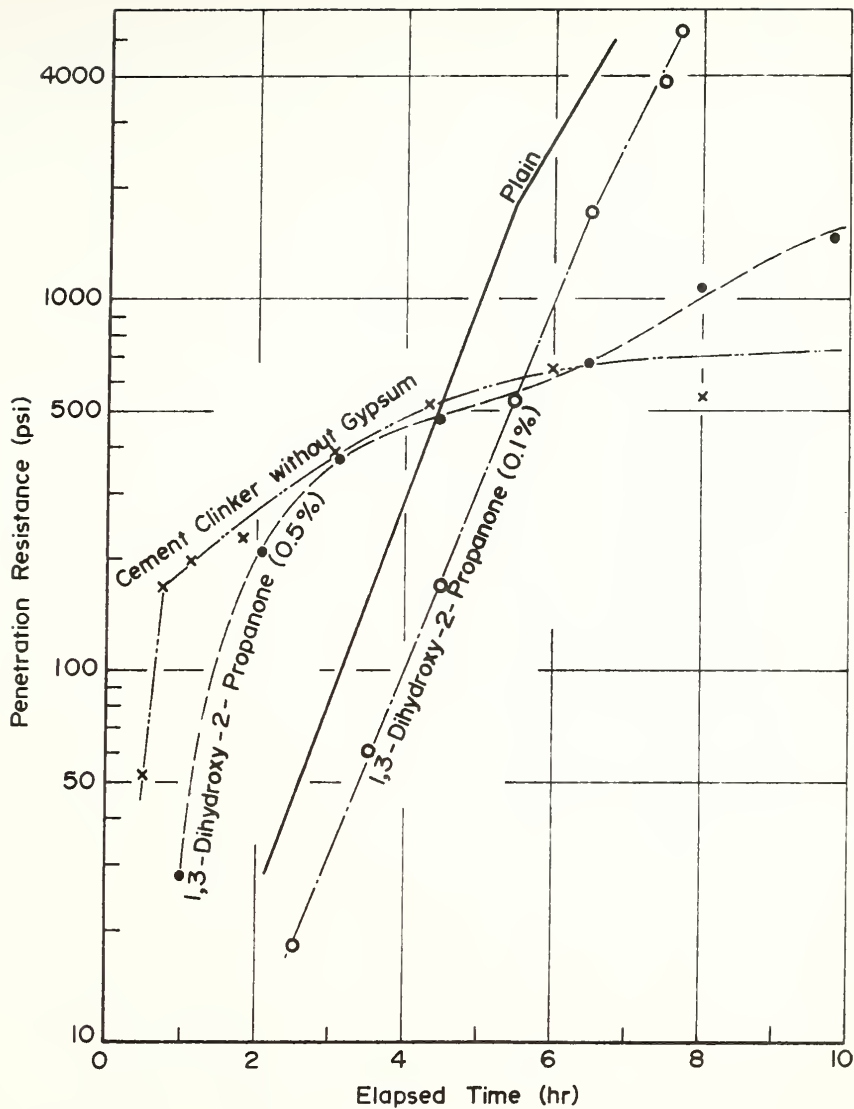


Figure 13 - Penetration Resistance vs Elapsed Time for Mortar with 1,3-Dihydroxy-2-Butanone

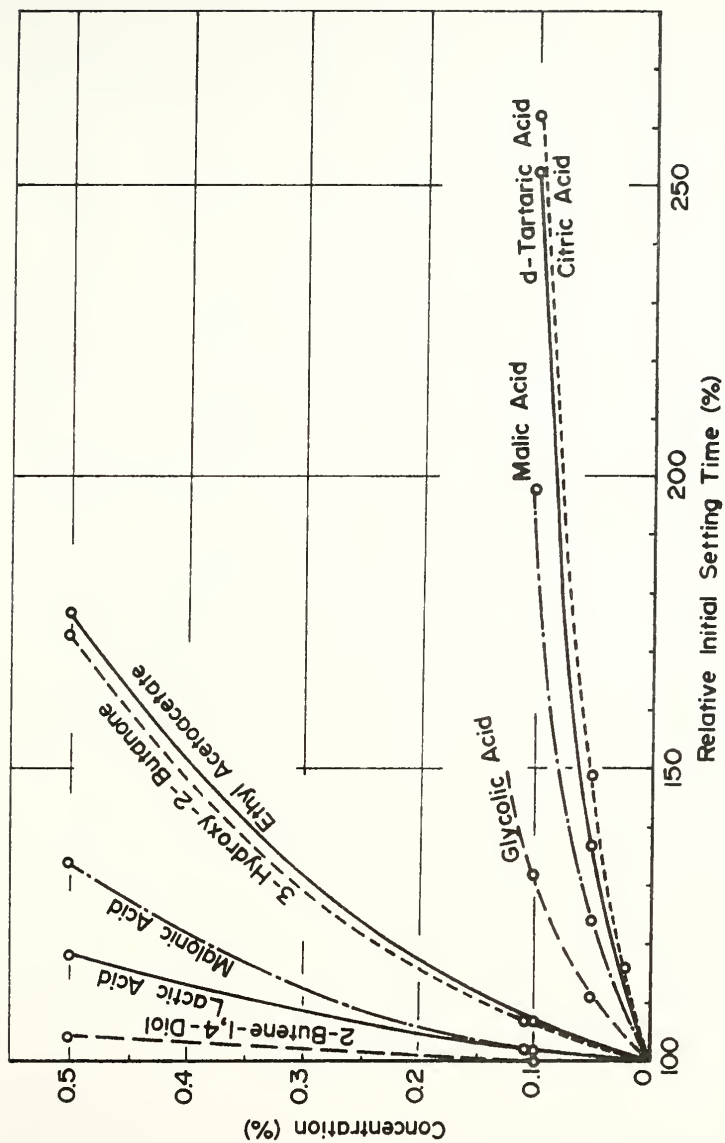


Figure 14 - Concentration of Admixture vs Relative Initial Setting Time of Mortar (No. 1)

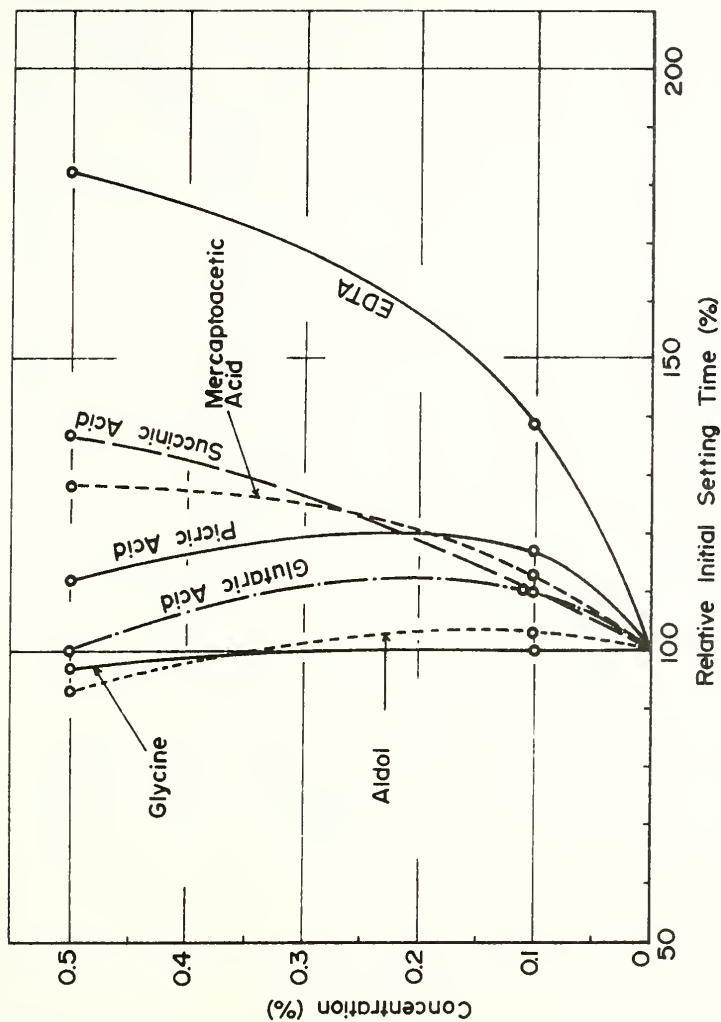


Figure 15 - Concentration of Admixture vs Relative Initial Setting Time of Mortar (No. 2)

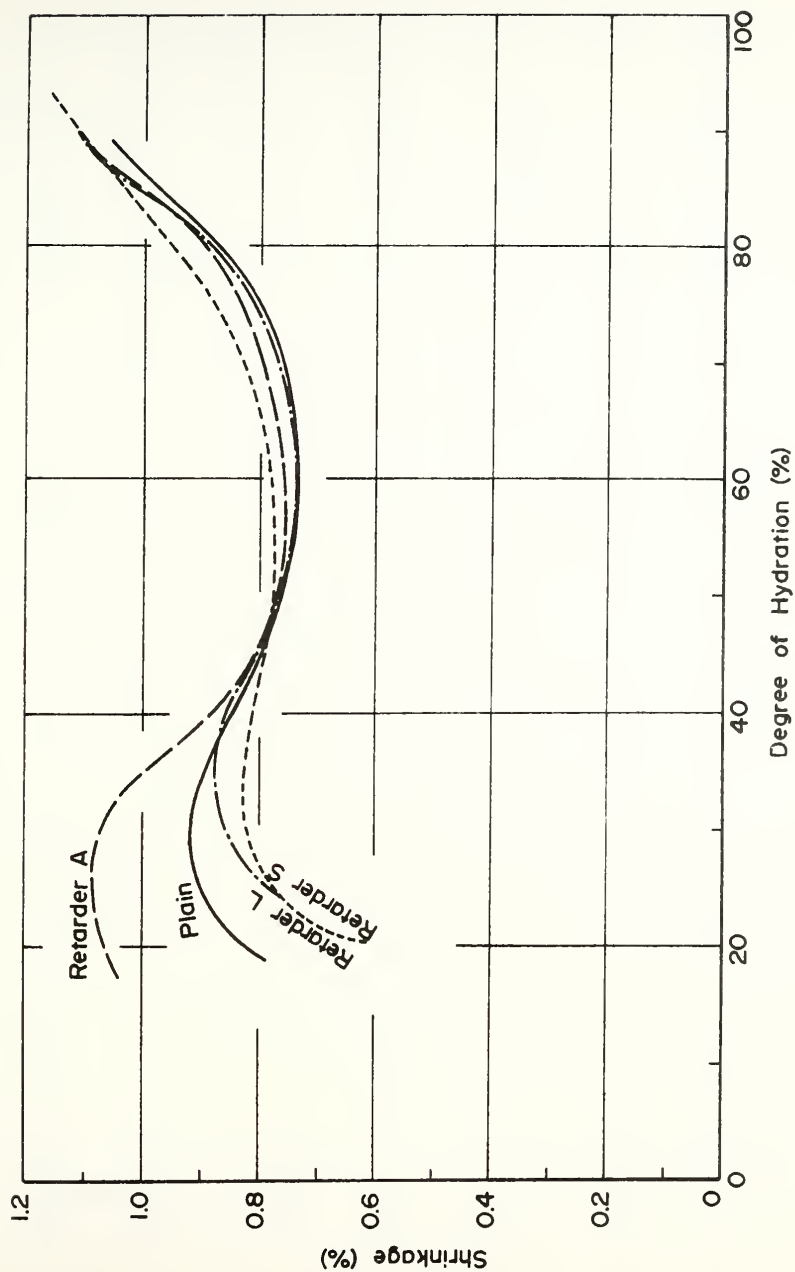


Figure 16 - Shrinkage of Vacuum Oven-Dried Cement Pastes at Various Stages of Hydration (Commercial Retarders)

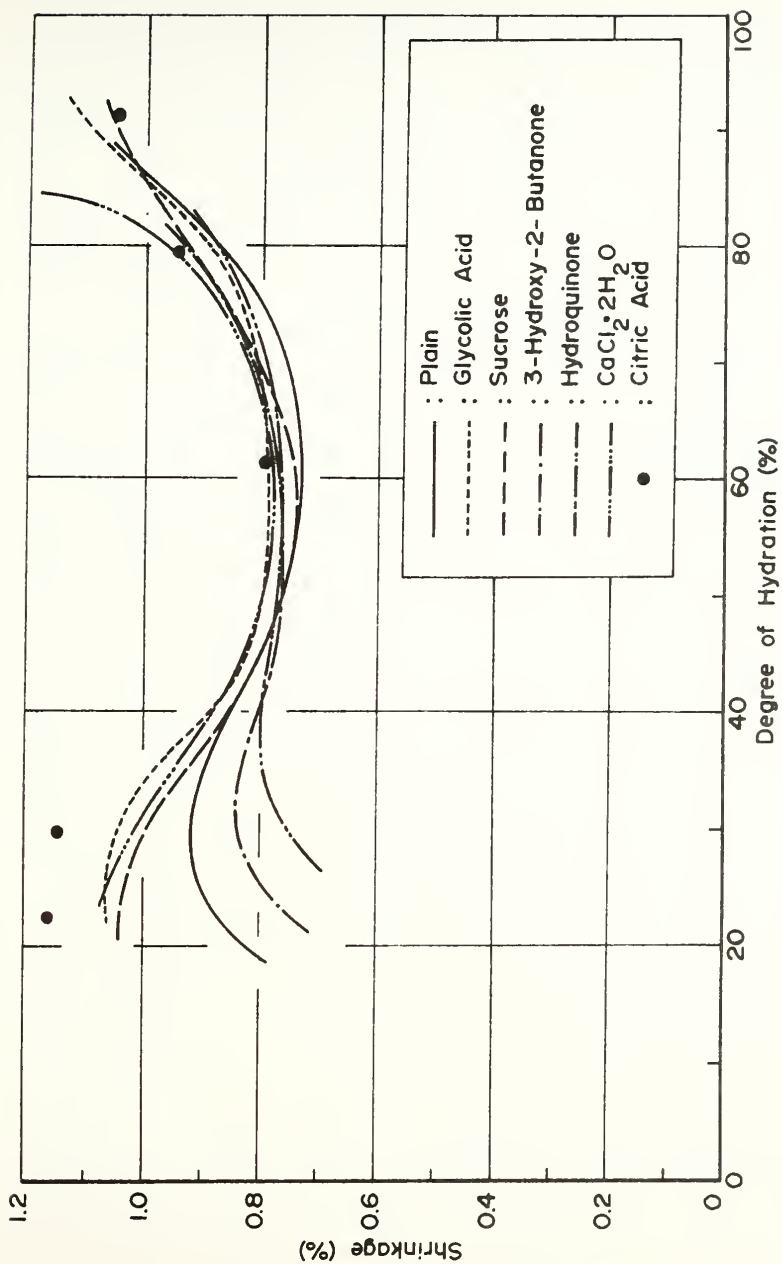


Figure 17 - Shrinkage of Vacuum Oven-Dried Cement Pastes at Various Stages of Hydration (Pure Chemicals)

against the degree of hydration of the samples, determined as previously explained. For clarity, data points are not shown in the figures. They are to be found in Appendix C. For citric acid, however, data points only are shown in Figure 17 because of the lack of enough points to draw a complete curve.

At the degree of hydration of about 50%, which roughly corresponds to an age of 2 days, all the samples shrank practically an equal amount, approximately 0.8%. The cement paste alone, with no admixture, always had a smaller shrinkage than the others at this point and at most later ages. At the degree of hydration of 85 to 90%, the rate of increase in shrinkage was reduced for all pastes except that with calcium chloride.

When the degree of hydration was between 20 and 45% the shrinkage behavior of the samples was changed significantly. All hydroxycarboxylic acids such as retarder A, glycolic acid and citric acid increased the shrinkage considerably. Sucrose had an effect about equal to that of these acids, but the carbohydrate retarder (S), conversely, minimized the shrinkage. The cement paste with lignosulfonate retarder (L) shrank more or less in the same way as did the cement paste with no admixture, but showed less shrinkage at early ages. Addition of 3-hydroxy-2-butanone or hydroquinone, which have no acid group, but only hydroxyl or carbonyl groups, resulted in a smaller shrinkage of

cement paste at this early age. Calcium chloride increased the shrinkage at all stages of hydration and showed the largest shrinkage of all hydrations higher than 50%.

When either the concentration of citric acid was increased enough to result in a relative retardation of 200% or the water-cement ratio of plain paste was changed from 0.40 to 0.43, the shrinkage of the pastes was practically unchanged. These results are to be found in Appendix C.

Drying Shrinkage of Mature Cement Pastes
When Dried at 50% Relative Humidity

Shrinkage of 10-months-old (i.e. almost mature) samples was measured over a period of 50 days in an atmosphere of 50% relative humidity. The results are shown in Figures 18 and 19. Each data point is the average of two separate measurements. The range of duplicate measurements was usually within 3% of the average. The commercial retarders and most of the chemicals of the hydroxycarboxylic acid type increased the shrinkage consistently. However, all the admixtures also increased the degree of hydration of cement paste at this age, and the samples did not reach the same degree of hydration. Instead, there is a tendency that a sample of higher degree of hydration shrinks more, as would be expected.

The relationships between shrinkage and weight loss of the samples are shown in Figures 20 and 21. If the

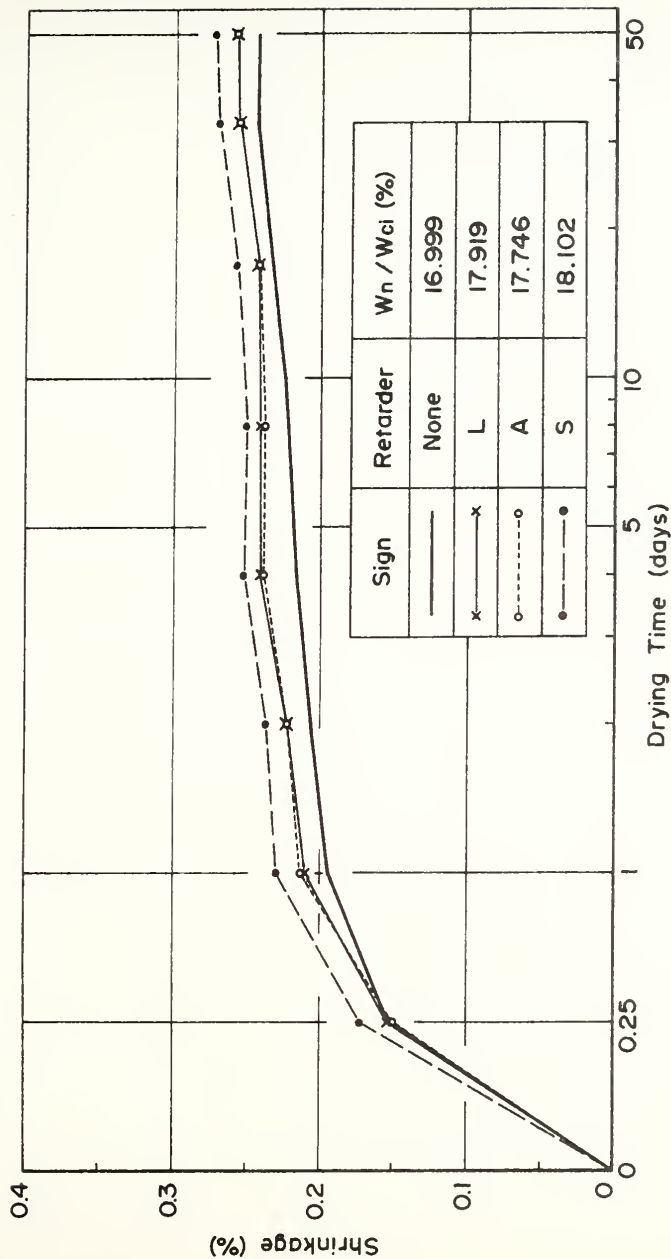


Figure 18 - Shrinkage vs Drying Time for Mature Cement Pastes When Dried at 50% Relative Humidity (Commercial Retarders)

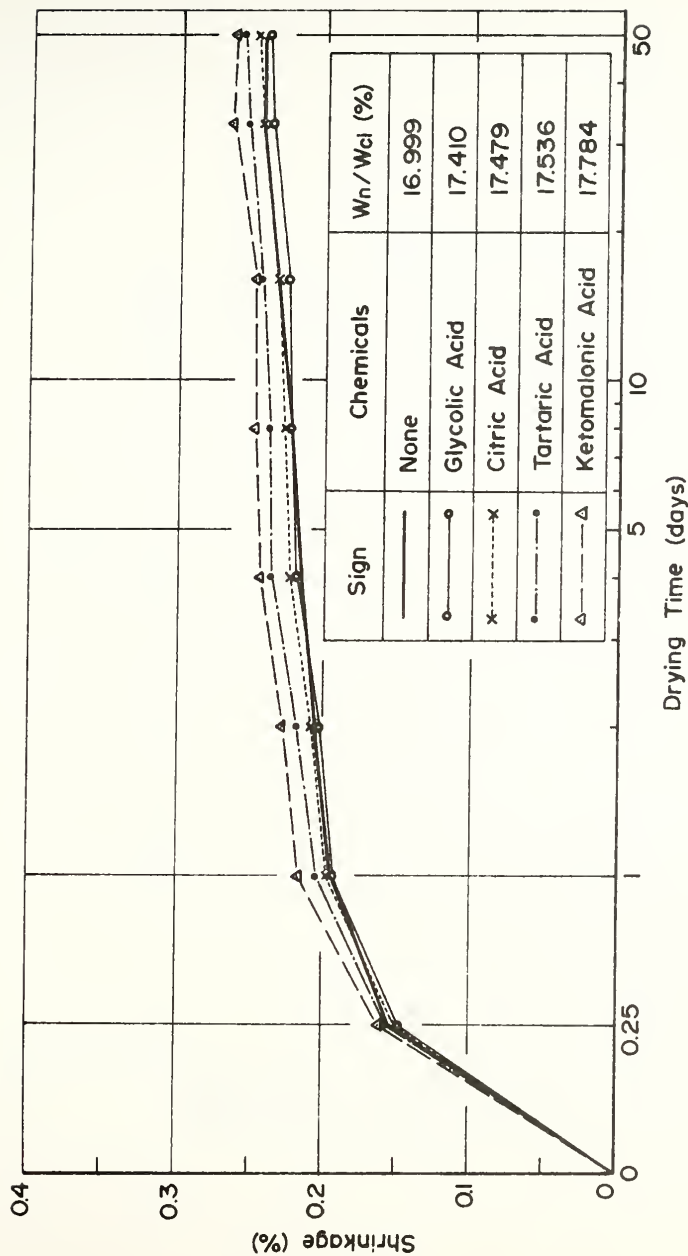


Figure 19 - Shrinkage vs Drying Time for Mature Cement Pastes When Dried at 50% Relative Humidity (Pure Acid Chemicals)

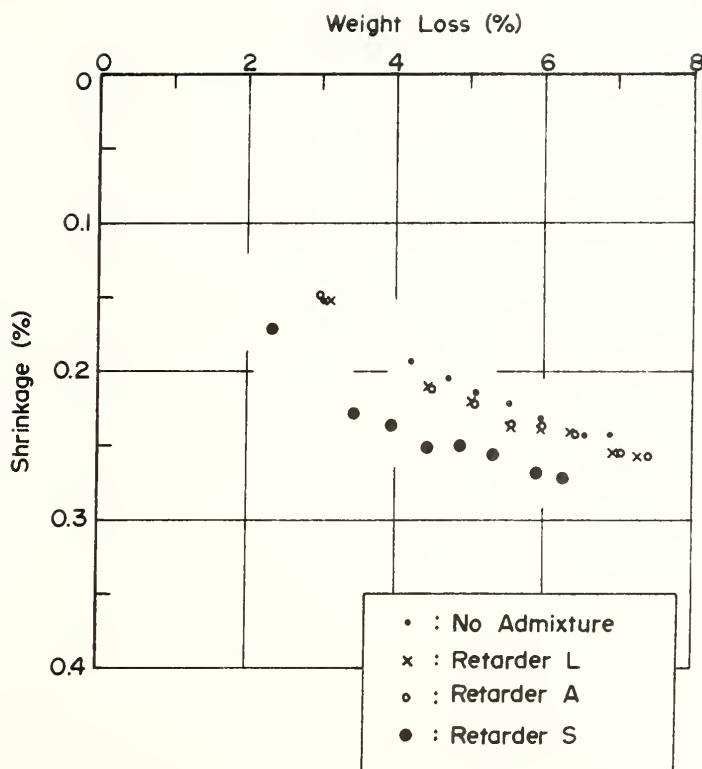


Figure 20 - Shrinkage vs Weight Loss of Mature Cement Pastes When Dried at 50% Relative Humidity (Commercial Retarders)

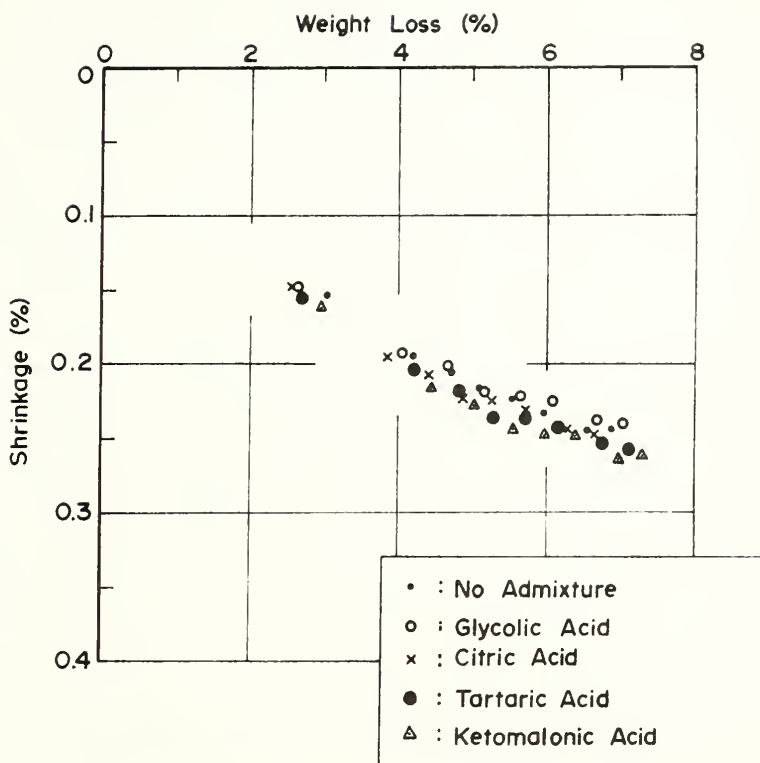


Figure 21 - Shrinkage vs Weight Loss of Mature Cement Pastes
When Dried at 50% Relative Humidity
(Pure Acid Chemicals)

weight loss in these figures is replaced by drying time in Figures 18 and 19, the relative position of each data point in both sets of figures appears to be the same. This similarity may be caused either by differences in the amount of hydration products produced or some change in the structure of the cement paste induced by the addition of the retarders. The cement paste with retarder S, however, showed extraordinarily large shrinkage when a certain amount of weight was lost. In this case, some changes in composition or structure of hydration products would be more expectable.

Water Content of Cement Pastes

Figures 22 and 23 show the relationship between evaporable water and non-evaporable water contents of cement paste samples. These water contents are expressed in percentage of original (i.e. dry) weight of cement, for ease of comparison. The original water-cement ratio of the samples was 0.40. The reason why the sum of W_n and W_e is greater than this is the increased water content brought about by self-desiccation and the efficient curing of these samples.

Each cement paste with a certain admixture shows its own relation in some different way from others. However, as indicated for the plain cement paste by solid lines, the data point could have scattered in a wide range if more measurements had been made. Yet, most of the points fall

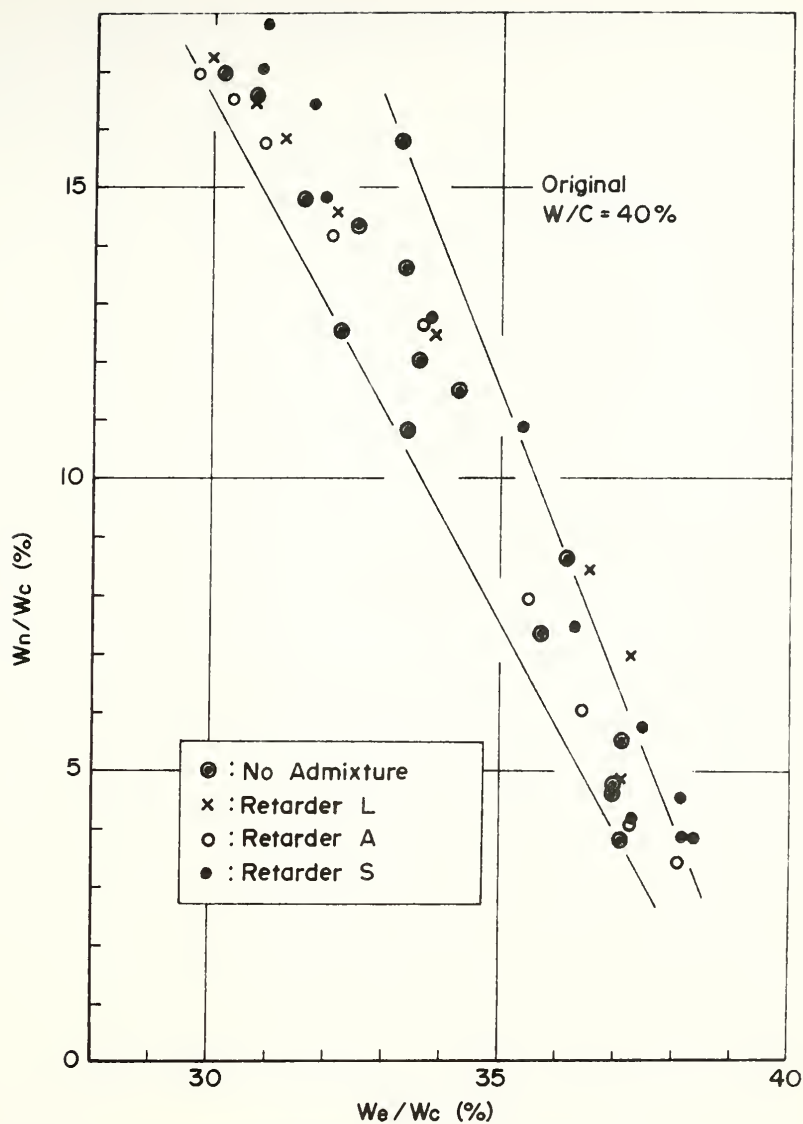


Figure 22 - Non-Evaporable Water vs Evaporable Water of Cement Pastes (Commercial Retarders)

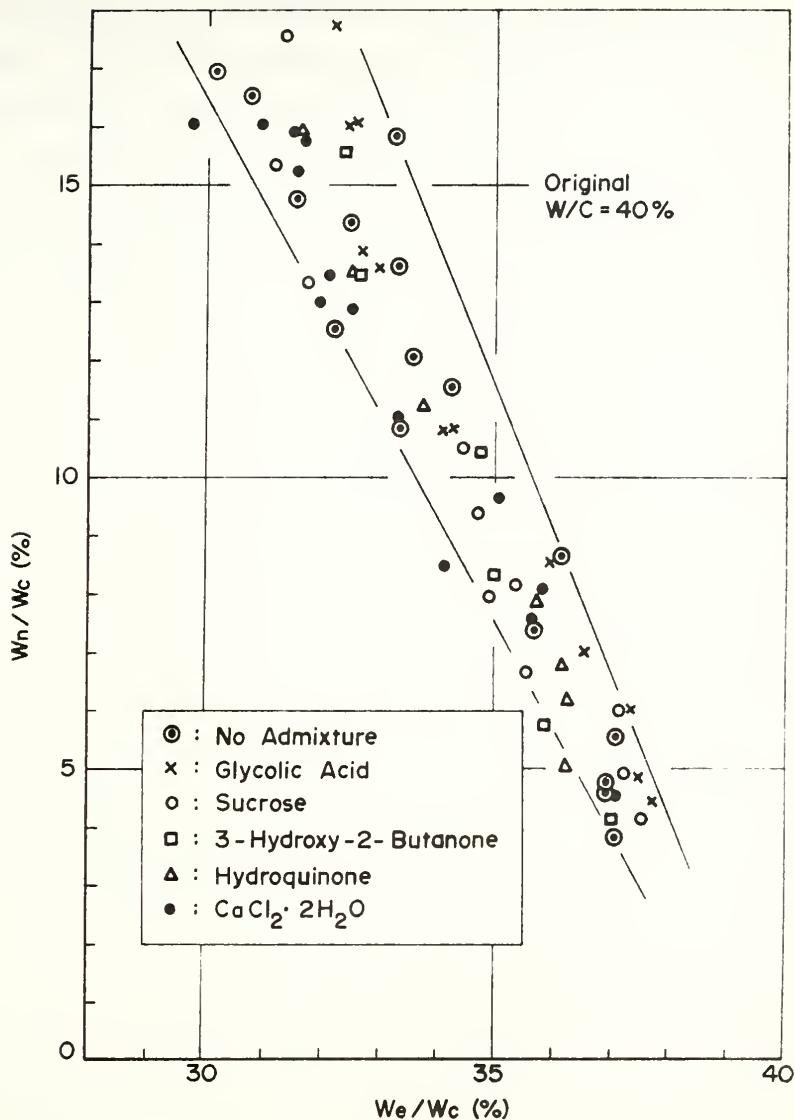


Figure 23 - Non-Evaporable Water vs Evaporable Water of Cement Pastes (Pure Chemicals)

in the region that the two lines for the control samples enclose. This could indicate that retarders do not change the structure of cement paste significantly.

In Figures 24 and 25, the non-evaporable water content is plotted against curing time of the samples. The solid line represents the relation for the cement paste without admixture. It can be seen that retarded degree of hydration of a cement by the addition of retarders at the concentration that results in relative set delay of 150% seems to be recovered completely in 2 to 4 days. After that, even some increase in the degree of hydration is observed for most pastes with retarders.

Specific Surface Area of Cement Pastes

The results of the water vapor adsorption experiments were used to calculate the specific surfaces of the paste samples. The calculation was done by means of the BET theory in the usual way and with the assumption of a unit area for the water molecule of 10.6 \AA^2 . The results are shown in Figures 26 and 27, on a basis of the ignited weight of the total sample. The values shown are averages of two measurements, which agreed to about 10%. As is expected, the larger the degree of hydration, the higher the specific surface area, and the relation is almost linear. However, there is no quantitatively noticeable difference observed among cement pastes with different admixtures.

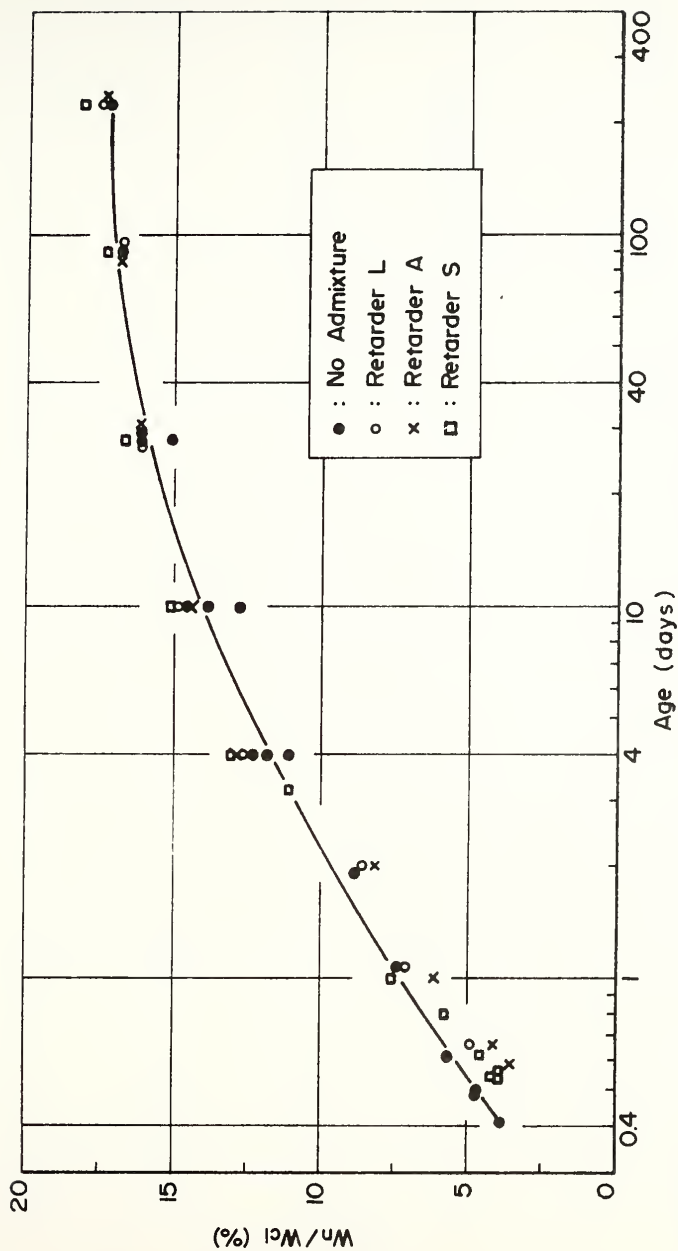


Figure 24 - Non-Evaporable Water vs Curing Age of Cement Pastes
(Commercial Retarders)

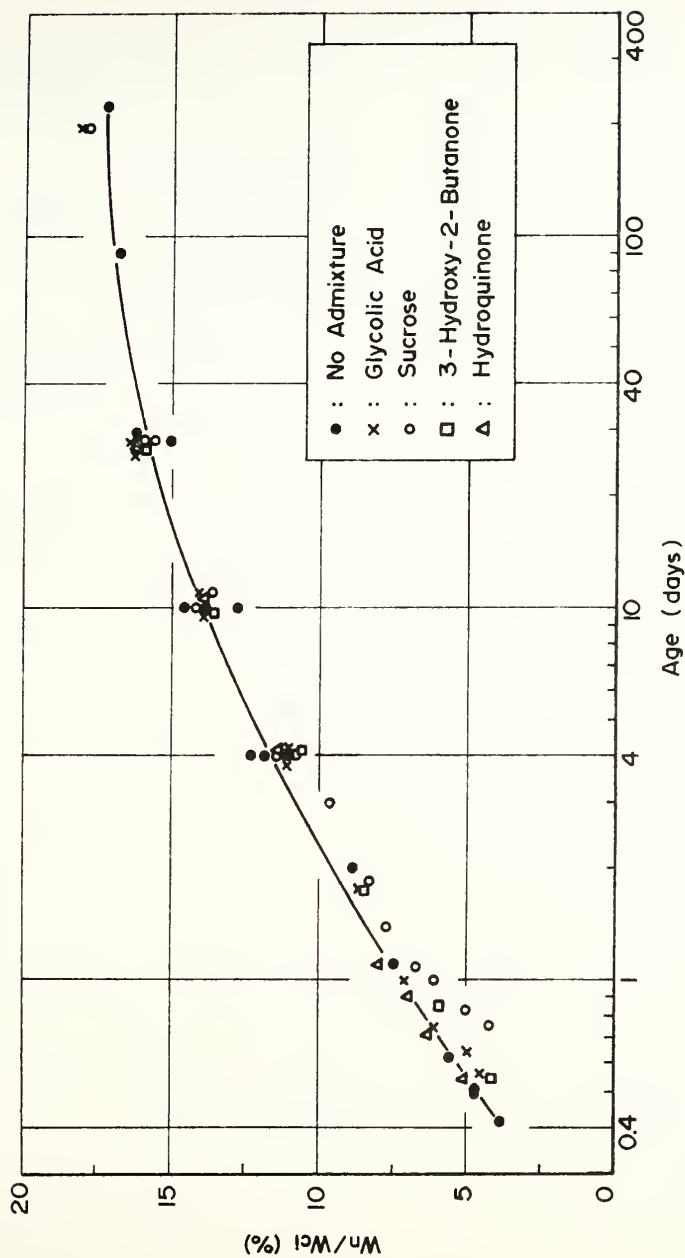


Figure 25 - Non-Evaporable Water vs Curing Age of Cement Pastes
(Pure Chemicals)

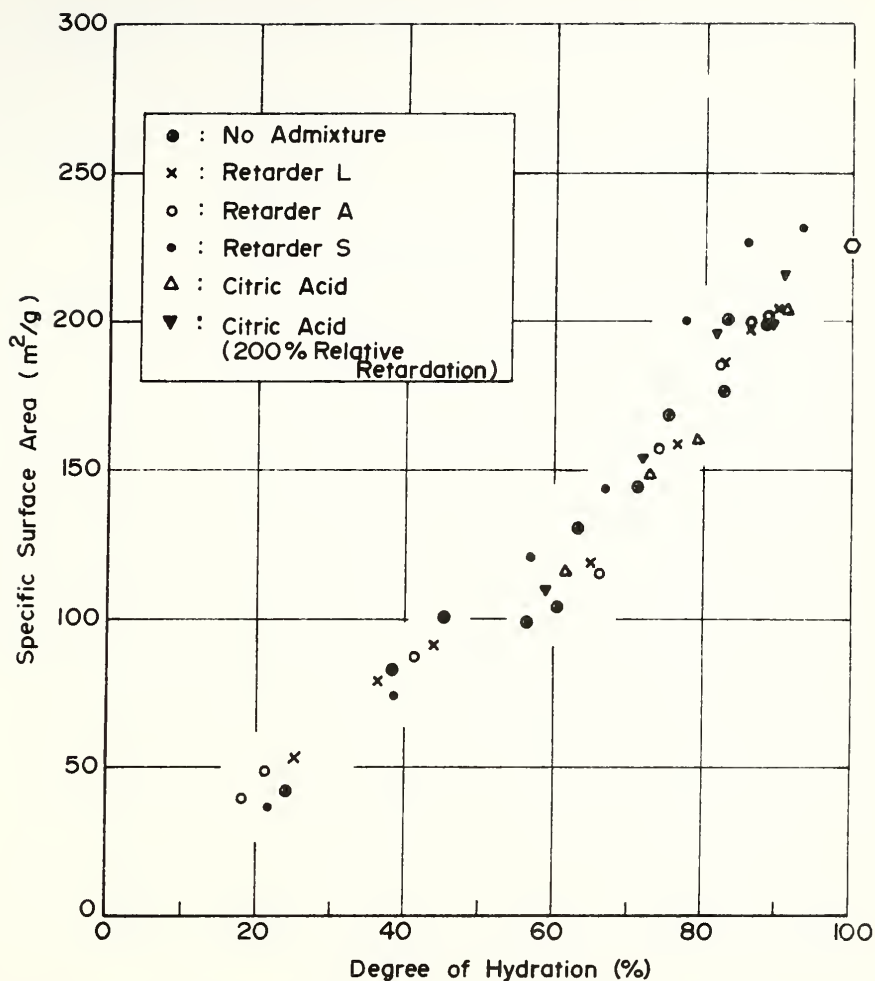


Figure 26 - Specific Surface Area of Vacuum Oven-Dried Cement Pastes When Expressed on the Basis of Total Ignited Weight of Samples (No. 1)

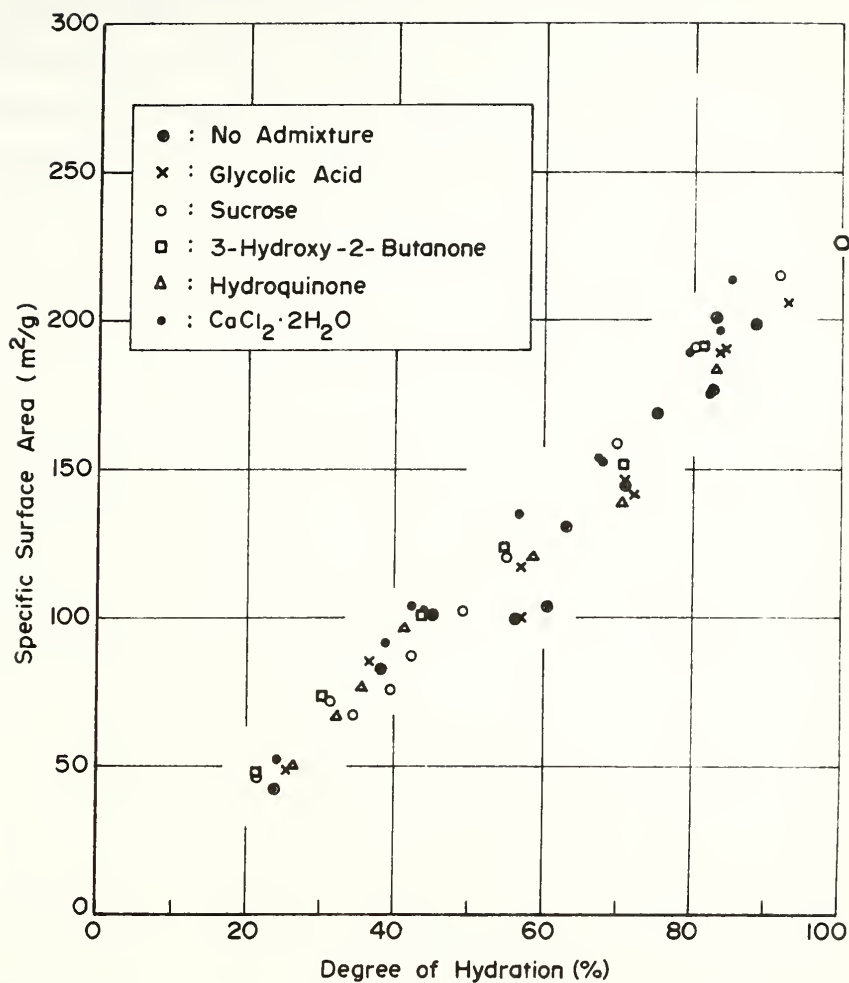


Figure 27 - Specific Surface Area of Vacuum Oven-Dried Cement Pastes When Expressed on the Basis of Total Ignited Weight of Samples (No. 2)

When specific surface area was expressed in terms of ignited weight of the hydrated portion of the sample, rather than the total sample, interesting curves were obtained. They are shown in Figures 28, 29, and 30. These curves are similar to those of the shrinkage results, shown previously. The samples that showed larger shrinkage at earlier age have also hydration products with larger surface areas at this age. At the degree of hydration of about 55 to 60% where the shrinkage curves showed a minimum, curves for surface area also show it, for the most part. Maximum specific surface area is attained when 85 to 90% of cement is hydrated, except for the sample with calcium chloride, and the surface area is reduced to some extent on further hydration. In the shrinkage curves, the rate of increase in shrinkage was also reduced at this degree of hydration. The cement paste with calcium chloride showed a strong increase in shrinkage at this stage and does so also in the surface area curve. The curves for sucrose and saccharide retarder (S) have a similar trend after more than 35% of the cement is hydrated. At earlier ages, however, sucrose increases surface area of hydration products remarkably as it did also the shrinkage of cement paste containing it. The only exception was the relatively young cement pastes with 3-hydroxy-2-butanone; they had hydration products of higher surface area, but shrank less than the others.

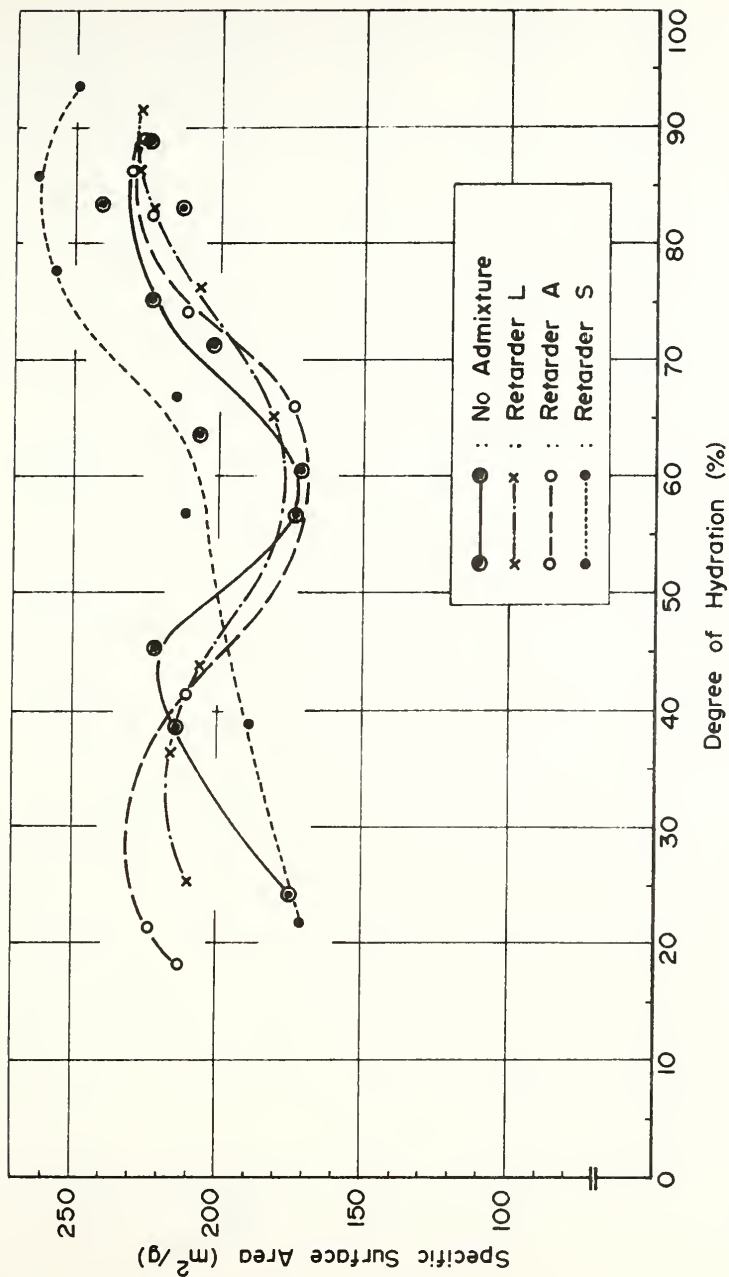


Figure 28 - Specific Surface Area of Hydrated Portion of Vacuum Oven-Dried Cement Pastes (Commercial Retarders)

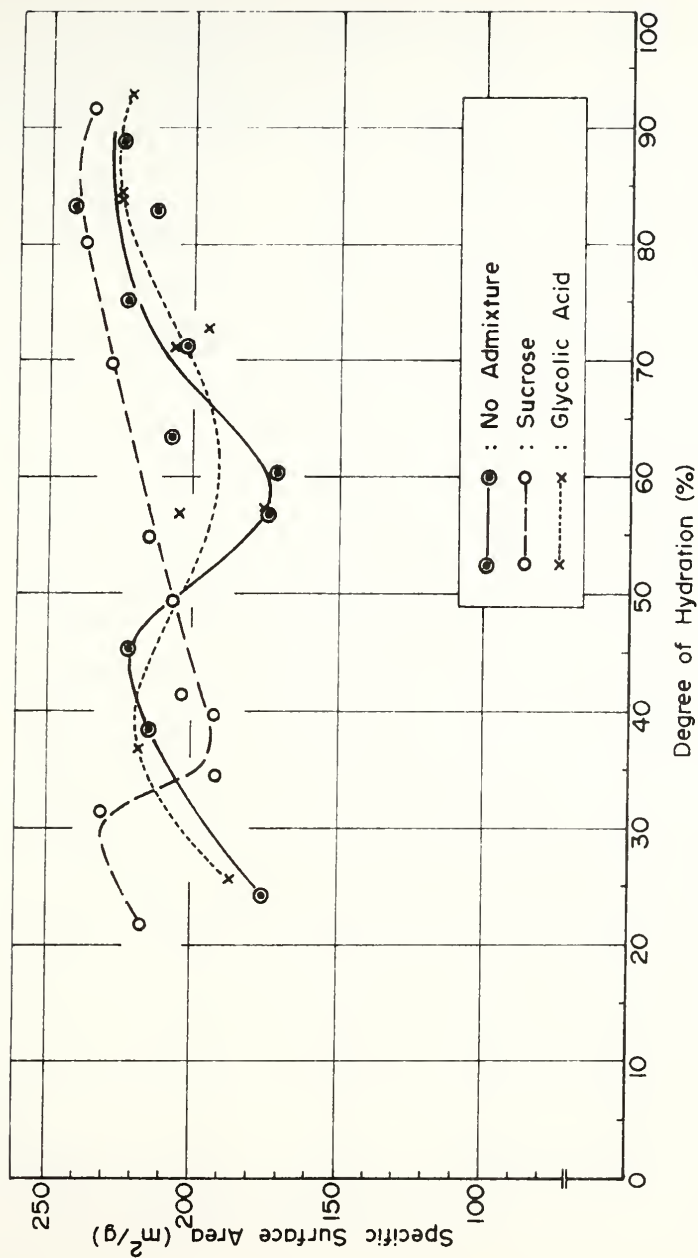


Figure 29 - Specific Surface Area of Hydrated Portion of Vacuum Oven-Dried Cement Pastes (Pure Chemicals - No. 1)

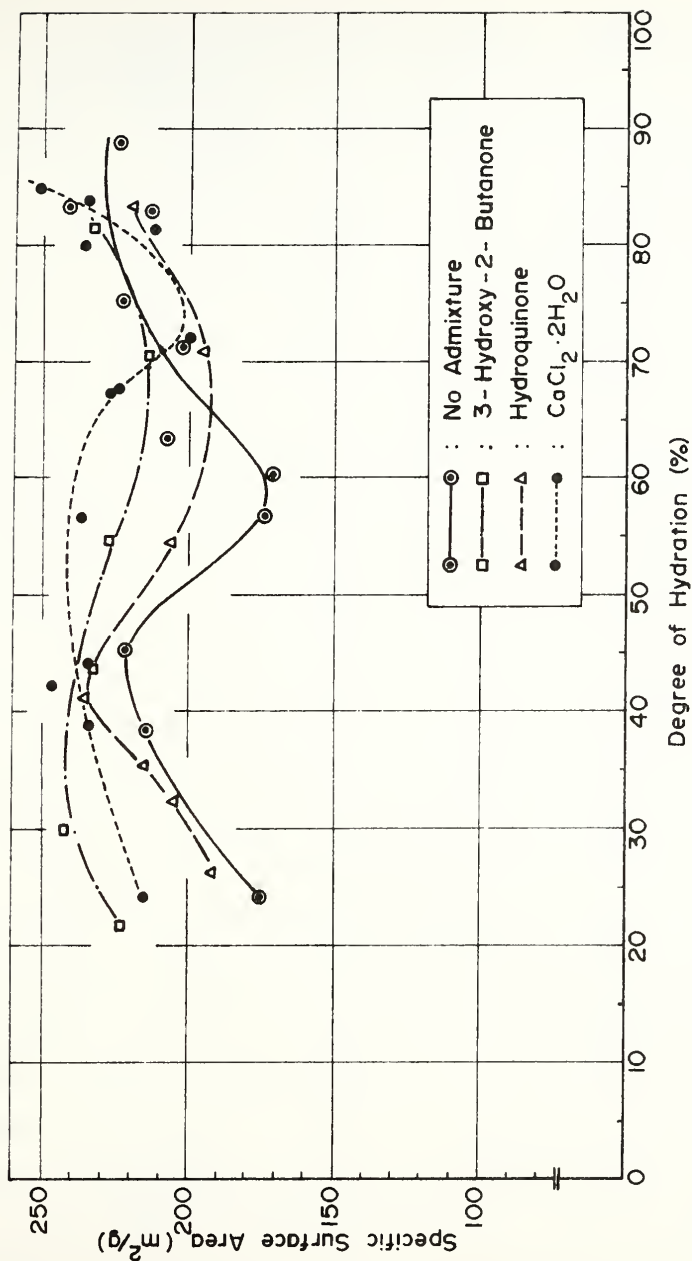


Figure 30 - Specific Surface Area of Hydrated Portion of Vacuum Oven-Dried Cement Pastes (Pure Chemicals - No. 2)

Scanning Electron Microscopy of Cement Pastes

Unhydrated cement grains seen through the scanning electron microscope are shown in Figure 31. Cement grains of various sizes ranging from 0.1 to more than 15 microns can be seen. Their surface texture looks smooth at this magnification. Figures 32 - 50 show pictures of hydrated cement pastes. Samples for Figures 32 - 46 were cast on glass, and the surface that faced the glass was observed after its removal by drying shrinkage. Concentrations of additives in these samples are those that yield a relative retardation of 200% in mortars. Figures 47 - 50 are photos of broken surfaces of samples that had been used for shrinkage measurements. Age shown is elapsed time or curing time before the sample was started to be dried in the oven.

At an elapsed time of 1 min, addition of retarders resulted in remarkable differences in the morphology of the hydration products. This can be seen in Figures 32 - 36. When no admixture was added, hydration products were observed on the surfaces of the grains. With calcium lignosulfonate added, the appearance of the product was changed; some particles were long and some were spherical. Their frequency seemed to be lower and their size larger. When citric acid was added, many needle-like crystals were seen. The needles were mostly observed to grow in a way so that several radiated from a point located either between large cement grains or sometimes from small grains



Figure 31 - Unhydrated Cement Grains (X5000)

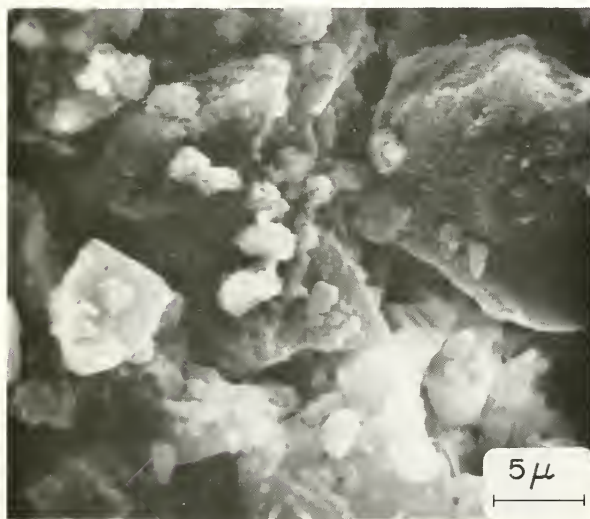


Figure 32 - Cement Paste with No Admixture (X3000)
Age: 1 min



Figure 33 - Cement Paste with No Admixture (X9000)
Age: 1 min



Figure 34 - Cement Paste with Calcium Lignosulfonate (X5000)
Age: 1 min



Figure 35 - Cement Paste with Citric Acid (X3000)
Age: 1 min



Figure 36 - Cement Paste with Sucrose (X5000)
Age: 1 min

of cement. EDAX analysis showed that these needles were composed of some silica, alumina, and sulfur and a large amount of calcium. It should be noted in the same figure that the surfaces of most of the cement grains remained relatively unchanged. In the sample containing sucrose irregularly shaped and rounded hydration products were seen on the surfaces of cement grains.

Photos of cement pastes at the age of 5 min are shown in Figures 37 - 40. More hydration had occurred in all samples. Most of the cement grains were covered with hydration product in the case of neat cement paste, and a hexagonal plate, which is probably a lime crystal, can be seen. The cement paste with calcium lignosulfonate still retained some rod-like projections. The long needles observed in the 1 minute citric acid sample tended to be fewer and seemed to be precipitated on the surfaces of the cement grains.

Figures 41 - 44 show that the long needles observed in citric acid samples at early ages disappeared as time elapsed. In the 10 minute sample, it is seen that most of the shortened needles were gone or transformed into rounded products on the cement grains. These round products look like those observed in 1 minute samples containing calcium lignosulfonate or sucrose. In 30 minute and 1 hour samples containing citric acid, no needle was seen, and the

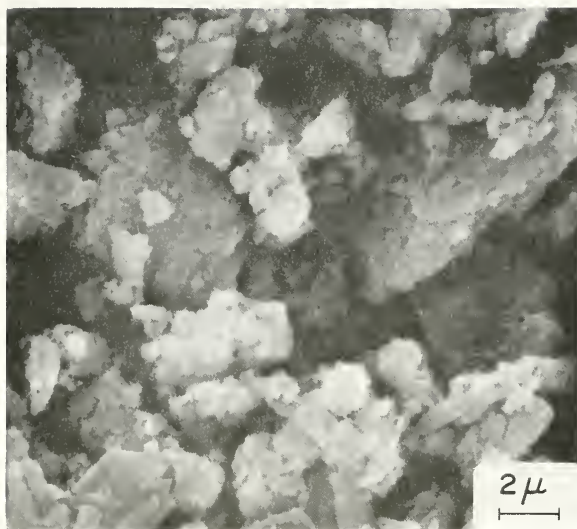


Figure 37 - Cement Paste with No Admixture (X5000)
Age: 5 min



Figure 38 - Cement Paste with Calcium Lignosulfonate (X5000)
Age: 5 min

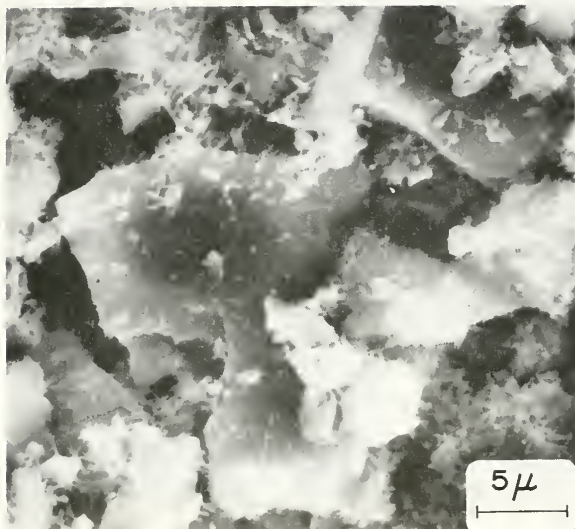


Figure 39 - Cement Paste with Citric Acid (X3000)
Age: 5 min

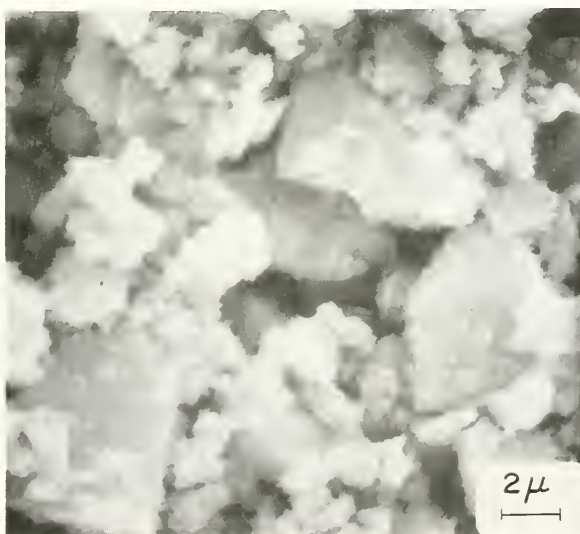


Figure 40 - Cement Paste with Sucrose (X5000)
Age: 5 min

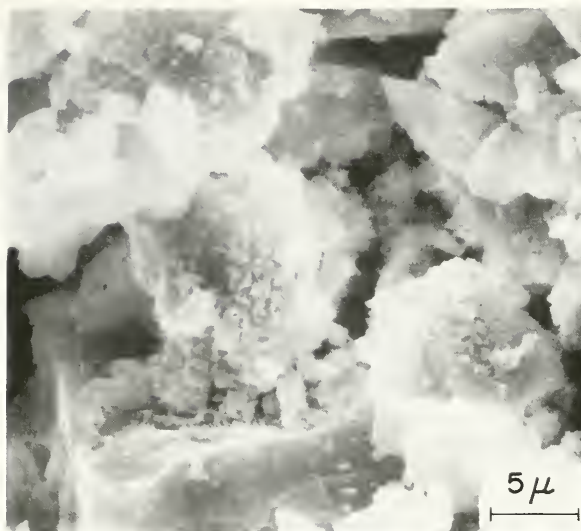


Figure 41 - Cement Paste with Citric Acid (X3000)
Age: 10 min



Figure 42 - Cement Paste with Citric Acid (X8000)
Age: 10 min

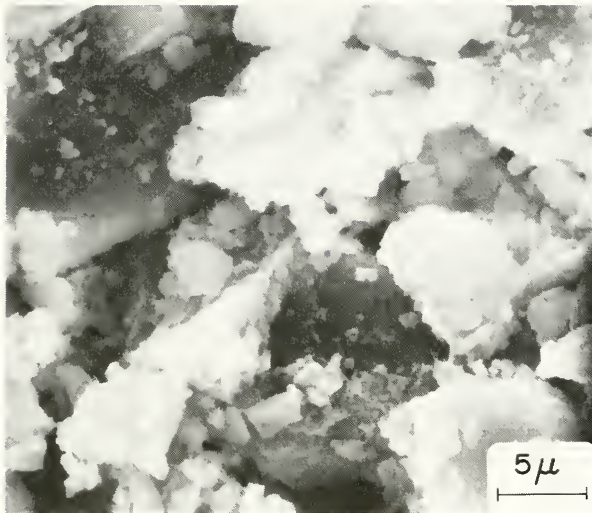


Figure 43 - Cement Paste with Citric Acid (X3000)
Age: 30 min

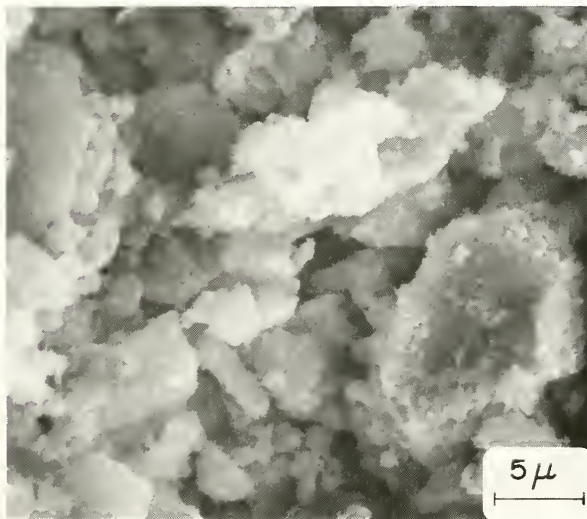


Figure 44 - Cement Paste with Citric Acid (X3000)
Age: 1 hr

transformed products continued to spread over the surface of the cement grains.

Figure 45 is a photo of a cement paste with no admixture after 1 hour. Cement grains appear to be covered by many grainy hydration products. The sucrose-containing sample at 30 min is shown in Figure 46 and is similar to the 1 hour sample containing citric acid.

Figures 47 - 50 show broken surfaces of cement pastes with and without retarders at ages of about half a day. The degree of hydration is also indicated. No noticeable difference is observed among the figures.

No photo is shown for cement pastes older than these samples in this thesis, because there was no notable difference observed regardless of the presence of retarders. Additionally, at ages later than 4 days, strong growth of lime crystals obscured the observation.



Figure 45 - Cement Paste with No Admixture (X5000)
Age: 1 hr

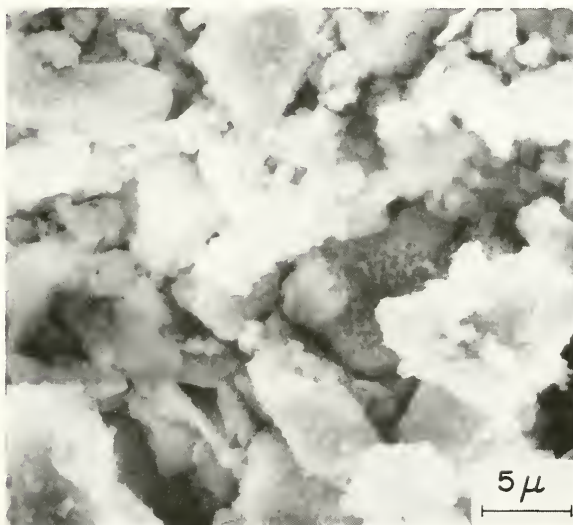


Figure 46 - Cement Paste with Sucrose (X3000)
Age: 30 min

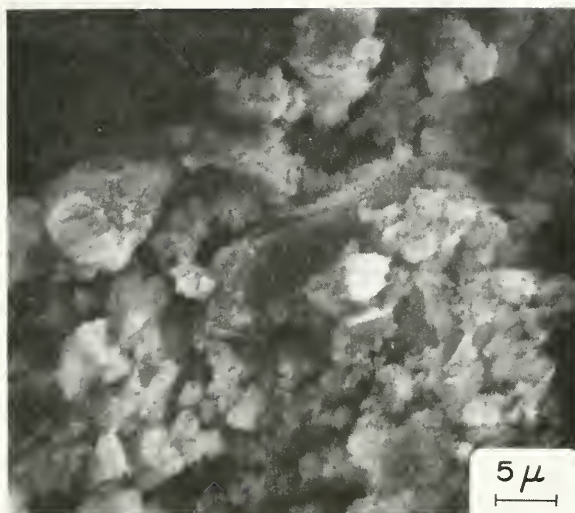


Figure 47 - Cement Paste with No Admixture (X2000)
Age: 12.5 hr
(degree of hydration: 24%)

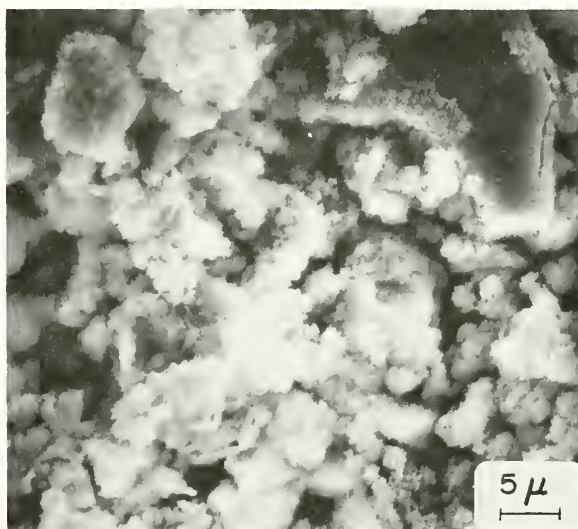


Figure 48 - Cement Paste with Glycolic Acid (X2000)
Age: 15.5 hr
(degree of hydration: 26%)

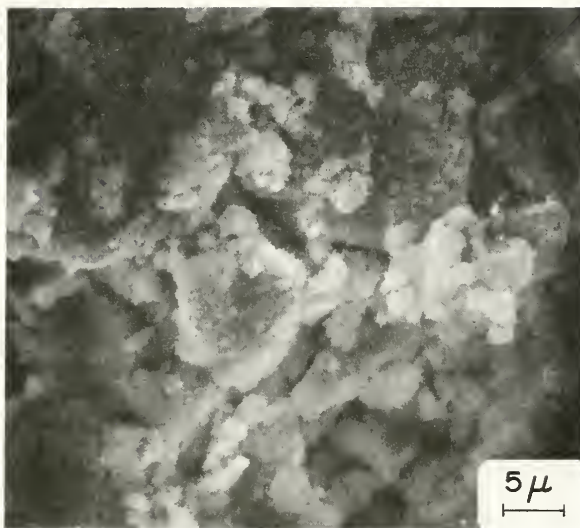
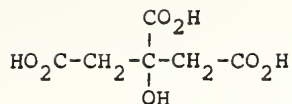


Figure 49 - Cement Paste with Retarder A (X2000)
Age: 14 hr
(degree of hydration: 18%)

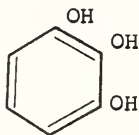


Figure 50 - Cement Paste with Retarder S (X2000)
Age: 13 hr
(degree of hydration: 20%)

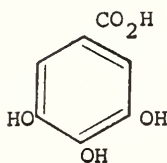
Citric acid



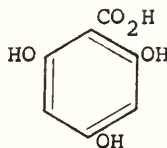
Pyrogallol



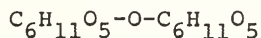
Gallic acid



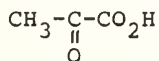
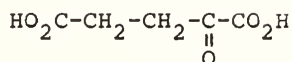
2,4,6-Trihydroxybenzoic acid



Sucrose

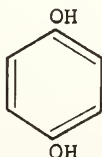


Pyruvic acid

and α -Ketoglutaric acid

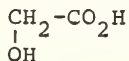
Of these, all are acids except sucrose and pyrogallol.

In connection with the latter compound it should be noted that hydroquinone



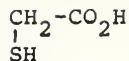
almost fell into the class of compounds listed above, with its relative retardation of 198%, and is also not an acid. The compounds listed above contain hydroxyl groups, usually many of them, and almost always, at least in aliphatic compounds, there is one in the α position to the $C = O$ of the carboxyl group. The only exceptions to these generalizations are the last two compounds in the list, pyruvic acid and 2-ketoglutaric acid. These two have a carbonyl group in the α position to the carboxyl group. This carbonyl group perhaps hydrates, to some extent, in solution to form a 2,2-dihydroxyl compound stabilized by the strong electron-withdrawing tendency of the adjacent carboxyl group. Another example of this condition is glyoxylic acid, which exists as the hydrate, even in the solid state. So these α -carbonyl compounds may qualify with respect to the hydroxyl group criterion, even though it is not apparent from the conventional formula.

The importance of the hydroxyl group is further emphasized by the changes that occur when it is exchanged for other groups. The relative retardation (T500) of glycolic acid

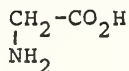


is 127%, a moderately strong retarder and the simplest example of an α -hydroxy acid. But if the hydroxyl group is exchanged for a sulfhydryl group, forming mercaptoacetic

acid

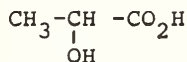


the T500 drops to 113% and for glycine

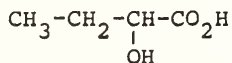


it is 100%, indicating no retarding action at all.

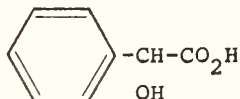
On the other hand, the presence of the hydroxyl group in the α position to the carboxyl group is not, in itself, sufficient for a compound to be a retarder. This conclusion is drawn from the insignificant retarding abilities of lactic acid



α -hydroxybutyric acid

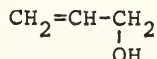


and mandelic acid,

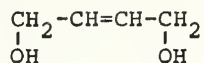


all of which are α -hydroxycarboxylic acids.

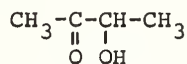
If the reason for the frequent efficacy of an α -hydroxy acid as a retarder is the activation of the hydroxyl group in the 3,4 position with respect to the double bond, then other compounds with a similar structure should behave similarly. Allyl alcohol



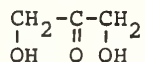
has no retarding ability; neither does 2-butene-1,4-diol,



but both have hydroxyls activated by the double bond. On the other hand, a carbonyl group does seem to have some effect, even if it is not part of a carboxyl group, as in 3-hydroxy-2-butanone

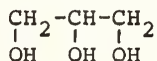


which has a T500 of only 107% at a concentration of 0.1% but 173% at a concentration of 0.5%. Another example is 1,3-dihydroxy-2-propanone

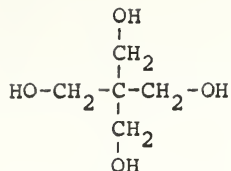


which has a value of 125% at 0.1%, but seems to act atypically, with a value of 97%, i.e. slight acceleration, at 0.5% concentration. The curve is, however, unusual. See Figure 13. These last two examples cannot be said to be strong retarders, although there is some action.

The presence of many hydroxyls is not, of itself, sufficient to confer retarding abilities on a molecule, as is shown by the result that glycerine

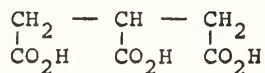


and pentaerythritol



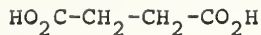
do not retard. Sometimes, however, strong retarders have only hydroxyls as functional groups, as has already been shown by the examples of hydroquinone and pyrogallol.

It is possible to have good retardation without the presence of the alcoholic hydroxyl group, as with 1,2,3-propanetricarboxylic acid

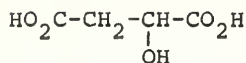


which had a T500 of 139, a value higher than that of glycolic acid. At the same time, it should be recognized that if the hydroxyl is not absolutely necessary, it is usually helpful in promoting retarding ability of a molecule; if the tertiary hydrogen in the above compound is replaced by a hydroxyl group, giving citric acid, the retarding ability is greatly promoted.

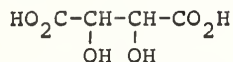
Other good examples of this effect involve the dicarboxylic acids. The acids malonic, succinic, glutaric, and adipic have only slight retarding ability at 0.1% concentration, although if five times as much is used, malonic and succinic acids have a respectable action. But the addition of hydroxyls greatly increases the retarding ability. At a concentration of 0.1% succinic acid



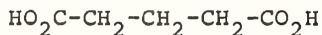
has a T500 of only 110%. The addition of only one hydroxyl to make malic acid



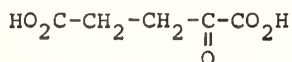
causes a great increase in a T500 of 198%. A second hydroxyl gives tartatic acid



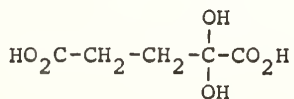
which has a T500 of 254% and is a powerful retarder. Glutaric acid



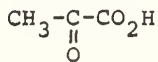
has a T500 of also only 110%, but 2-ketoglutaric acid



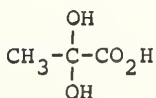
which may, as previously mentioned, exist as



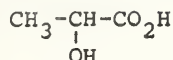
in solution, has a T500 of 292%, one of the highest values measured. A similar effect is observable with pyruvic acid



or

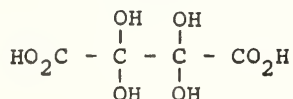


which is a strong retarder with a T500 of 207%, whereas the mono-hydroxy counterpart, lactic acid

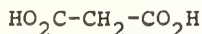


has no retarding ability at all at 0.1% concentration and not much at 0.5% (T500 = 118%).

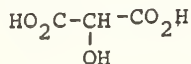
Sometimes, however, more hydroxyls seem to be too much of a good thing. For example, dihydroxytartaric acid



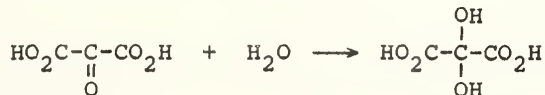
is not as good a retarder (T500 = 166%) as tartaric acid (T500 = 254%), although it is still a strongly active substance. The same effect is observed with the hydroxy derivatives of malonic acid,



which has a T500 of only 102%. Addition of one hydroxyl group gives tartronic acid



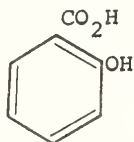
which is a powerful retarder with a T500 of 278%. A second hydroxyl gives the hydrate of ketomalonic acid



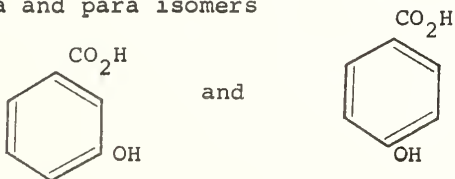
which is still a strong retarder, with a T500 of 154%, but is not nearly so strong as tartronic acid.

From the above it is apparent that the hydroxyl group is frequently found in retarder molecules and is frequently α to a carbonyl, but that this structure alone, or the plain hydroxyl alone, is not sufficient in itself to confer a high retardation ability on a molecule.

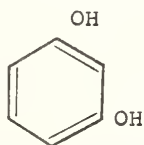
Influences of molecular structure are observable also with respect to the different retarding abilities of position isomers. Salicylic acid, which has been recognized as a set retarder for some time, has a T500 of 122%. It is o-hydroxybenzoic acid.



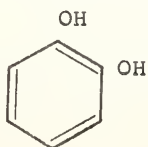
But the meta and para isomers



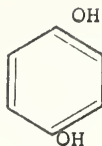
had practically no retarding ability. Of the three dihydroxybenzenes, resorcinol, the meta isomer,



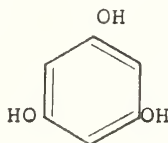
is not a retarder, but the ortho isomer, catechol



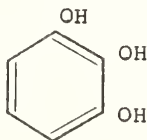
is a fairly good retarder, with a T500 of 127%, and the para isomer, hydroquinone,



is better yet, with a T500 of 198%. It is, of course, usual for ortho and para isomers to be alike in chemical properties and different from the meta compound. Another example is the trihydroxybenzenes. Phloroglucinol, 1,3,5-trihydroxybenzene,



has a T500 of 131%, a fairly good retarder, but pyrogallol, 1,2,3-trihydroxybenzene,



is much stronger, with a T500 of 239%.

From this discussion certain generalities can be inferred empirically with respect to the molecular structures that characterize retarders. They are frequently carboxylic acids, but need not be necessarily. They frequently contain many hydroxyl groups, but need not necessarily. The hydroxyl is frequently in the α position

to the carboxyl. And some compounds containing most of these features are not especially good retarders.

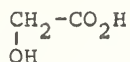
All the really strong retarders used here are highly oxygenated substances. The oxygen atoms can be in hydroxyl, carboxyl, or carbonyl groups; all seem to be effective, although some are, no doubt, more so than others. The oxygen atoms are also usually fairly well spread out across the molecule. That is, significant portions of the molecule devoid of oxygens seem to lessen the retarding ability as, for example, with the dicarboxylic acids, lactic acid, and α -hydroxybutyric acid. The strong retarders, furthermore, usually contain several oxygen atoms that can, by virtue of their location on the chain and rotations about single bonds, approach each other closely and form a "cluster" of oxygen atoms. In this connection, it should be remembered that chain structures are kinked at tetrahedral angles, so the usual formula as written is not a particularly clear indication of the real spatial relationships in the molecule.

The foregoing notions, of course, merely repeat to some degree the older postulates of Hansen (24), Steinour (25), and especially Taplin (27).

Deserving perhaps of special comment is the seemingly great strength of the α -carbonyl group. All substances tested that have carbonyls adjacent to carboxyl groups -

pyruvic acid, ketomalononic acid, and 2-ketoglutanonic acid, were strong retarders.

One can go a little further and say "Why oxygen?" Why will not other groups function just as well? But it seems that the oxygen atom in one form or another is almost uniquely required for the retarding action. For example, glycolic acid

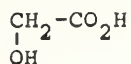


is a fairly good retarder, but mercaptoacetic acid, glycine, and monochloroacetic acid in which the hydroxyl has been exchanged for -SH, -NH₂, and -Cl, respectively, are all poor or completely ineffective as retarders.

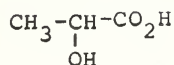
The properties of the oxygen atom that seem most likely to be of consequence are its high electronegativity, its consequent ability to participate in strong hydrogen bonding with other electronegative atoms, its small size, and its presence in the molecules of both the liquid phase of concrete and the surfaces of the anhydrous cement minerals and of their hydration products.

It may be that one important function of the highly electronegative oxygens is to bring about electron shifts in the retarder molecules and induce charge polarizations that could determine the adsorption characteristics of the molecules on the charged solids present.

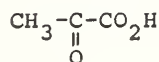
For example, consider the differences between glycolic acid,



lactic acid,



and pyruvic acid,



It should first be emphasized that in the relatively highly basic medium of cement paste or concrete (about pH=12.5) the carboxyl hydrogen atoms of all these weak acids will be dissociated, leaving the anion as the species really present in the aqueous phase.

In glycolic acid it can be postulated that small local positive charges are generated on the carbons or the hydrogens by the polarizing power of the various oxygens. Lactic acid is an extremely weak retarder, regardless of the fact that it has only a methyl group attached to the second carbon in place of the one hydrogen atom of glycolic acid. On the contrary, pyruvic acid which has one oxygen attached to the second carbon by a double bond, instead of the hydroxyl group of lactic acid, retarded the hydration of cement strongly. As has already been noted, the pyruvic acid may hydrate in aqueous solution to give the dihydroxy compound with both groups on the alpha carbon atom.

In pyruvic acid the double bonded oxygen or the oxygens in the hydroxyl groups, as the case may be, may pull the electrons around the third carbon toward the second carbon and polarize the hydrogen atoms on the third carbon atom. This trend may be further promoted by the oxygens in the acid group. This kind of polarizing effect on the hydrogens in the methyl group would be expected little for the lactic acid molecule, although the hydrogen of the second carbon could be subjected to the effect, mainly by the double bonded oxygen in the acid group and partially by the oxygen in the hydroxyl group.

When one hydrogen of the third carbon of lactic acid is replaced by another methyl group, the result is α -hydroxybutyric acid, which was not a retarder. However, if the end methyl group of lactic acid or α -hydroxybutyric acid is replaced by an acid group, the strong retarders tartronic acid and malic acid, respectively are made. Possibly all the hydrogens of the latter two chemicals could have the aforementioned polarizing effect. Hence, it appears that perhaps the movement of electrons should be considered in seeking the effective molecular structure of retarders.

The question of the relative locations of hydrogen atoms and atoms of high electronegativity (usually oxygen) arises next. The dicarboxylic acid compounds - malonic, succinic, glutaric and adipic acids - have an acid group

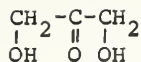
at each end of the molecule, but no hydroxyl groups. The former two are weak retarders when added at relatively high concentrations, while the latter two are not retarders at all. If the differences in retardation powers of these chemicals are caused by the polarizing effects of the carboxyl groups on nearby hydrogens, the result would indicate that at most only two hydrogens attached to the second carbons could have the influence to some extent.

Following this logic, it can be concluded that the greater retarding abilities of the compounds in which hydroxyl or carbonyl groups lie along the chain between the acid groups (tartronic, ketomalonic, malic, tartaric, dihydroxytartaric, 2-ketoglutaric, and mucic acids) are due, at least partly, to the increased polarization effects of these groups on the other atoms in the chain, effects which are lacking in the simple acids.

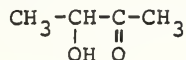
For the oxygen in the hydroxyl group, the extent of this effect is found by comparing the above result and the molecular structures of the chemicals already referred to. Lactic acid was an extremely weak retarder. 3-Hydroxypropionic acid and α -hydroxybutyric acid were not retarders. Hence, the hydroxyl oxygen atom could have this effect on only the one hydrogen atom attached to the same carbon. The hydrogen atom in the hydroxyl group would be, of course, also polarized.

If these ideas are applied to the glycine molecule, the reason why it is not a retarder may be also explained. The nitrogen of glycine has two hydrogens bonded to it, but it has lower electronegativity than oxygen. Therefore, the nitrogen may not have enough ability to polarize even one hydrogen bonded to the second carbon atom. Additionally, the polarizing effect per hydrogen which is bonded directly to the nitrogen would be less than half of that of the hydrogen in hydroxyl group, and the resulted polarization might not be strong enough to permit the substance to act as a retarder. The small retarding ability of mercapto-acetic acid, compared with glycolic acid, can be also explained by the considerably lower electronegativity, therefore the polarizing effect, of sulfur than oxygen.

The discussion so far given is confined to several chemicals. The idea can be generalized; that is, the molecular configuration of effective retarders is that atoms in the molecule are arranged in such a way to polarize as many hydrogen atoms as strongly as possible. Oxygen atoms are mainly responsible for the polarizing process because of their high electronegativity and low valence. However, it should be noticed that the effective configuration does not necessarily require carboxylic acid groups. If the idea is correct, it should be able to be generalized, at least somewhat. The modest retarding abilities of 1,3-dihydroxy-2-propanone



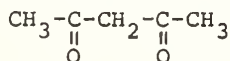
and 3-hydroxy-2-butanone



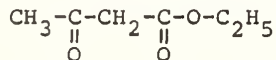
are examples of such generalization.

The rationality of these ideas is further supported by the fact that the electrogenativities of hydrogen, carbon, sulfur, nitrogen, and oxygen are 2.1, 2.5, 2.5, 3.0, and 3.5, respectively. The larger the difference in electronegativity between two atoms, the more ionic is the bond. Therefore, stronger polarizing effect would be expected for O-H combination than for N-H or S-H combination.

These ideas are, furthermore, subject to semiquantitative verification. For example, 2,4-pentanedione



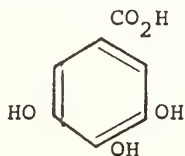
and ethyl acetoacetate



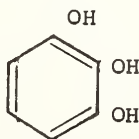
are both mild retarders, as would be expected from the strong polarizations of only the methylene hydrogens. Generally, little retardation is expected unless more than two-thirds of the hydrogens in a molecule are polarized evenly throughout the molecule and the polarizing effect is strong enough.

However, it should be noticed that the relative effectiveness of some compounds, e.g. tartaric, dihydroxy-maleic, and dihydroxytartaric acids, can not be explained by these ideas. Also, ketomalonic acid should have been a stronger retarder than tartronic acid, because the middle double bonded oxygen of ketomalonic acid will be opened in water and will form two hydroxyl groups. These apparent contradictions were probably caused by the many other physical and chemical influences of chemicals in cement paste.

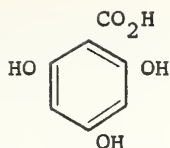
What has been said previously has dealt with the aliphatic compounds tested. The aromatic compounds also show many of the same features, as well as interesting effects of structural isomerism mentioned earlier. The strong aromatic retarders are all highly oxygenated and the strongest retarders, gallic acid



pyrogallol



and 2,4,6-trihydroxybenzoic acid



all have groups of oxygen atoms that approach each other closely. In this connection, it should be recalled that most of the hydrogen atoms of strong aliphatic retarders are polarized strongly by many oxygen atoms and that these oxygen atoms are usually located in such a way that they also approach each other closely.

Benzoic acid is not a retarder, nor is its meta or para hydroxy acid, but salicylic acid is a moderate retarder. Since the hydroxy group of salicylic acid is located on the second carbon from the acid group, it might seem that it would be analogous to the non-retarding 3-hydroxypropionic acid. But the latter is a much more flexible molecule with configurations in which the hydroxyl and carboxyl are relatively removed from each other, whereas in salicylic acid the two groups are constrained to proximity and also tied together by their intramolecular hydrogen bond.

The trihydroxybenzenes are good retarders, but pyrogallol, in which the hydroxyls are in adjacent positions on the ring, is a much stronger retarder than is phloroglucinol, in which they are separated. Converting either to its acid improves the retardation ability still further.

Gallic acid (3,4,5-trihydroxybenzoic acid) is an even stronger retarder than is 2,4,6-trihydroxybenzoic acid.

The three dihydroxybenzenes present an apparent exception to the generalization involving contiguous hydroxyls or oxygen atoms. The ortho isomer, catechol, is a fair retarder, while the meta isomer, resorcinol, is not active at all. But the para isomer, hydroquinone, in which the hydroxyls are separated to their greatest extent, is the best of all, with a T500 of 198%.

The findings of this study agree generally with those of Steinour (25, 26) with respect to the importance of hydroxyl groups and of Taplin (27) with respect to the importance of the hydroxyl adjacent to a carbonyl group. But, as mentioned earlier, glycerin and pentaerythritol are not retarders in spite of many hydroxyl groups. Propanetricarboxylic acid is a good retarder with no alcoholic hydroxy groups; citric acid is very strong with only one. Lactic and mandelic acids fulfill Taplin's criteria, yet they are not good retarders, and so on. There are so many exceptions that it is clear the older generalizations must leave out important aspects of the problem.

Effect of Retarders on the Hydration of Cement

In an effort to explain some of the ways in which retarders influence the hydration of portland cement,

some facts concerning the process need to be reviewed briefly.

The principal active components of portland cement at early stages of hydration are C_3S and C_3A . Through the hydration of C_3S , calcium silicate hydrate is formed and lime is released into solution in the form of Ca^{++} and OH^- . C_3A , on the other hand, reacts with sulfate and calcium ions from the solution to form ettringite, $C_3A \cdot 3\bar{CS} \cdot H_{32}$.

In a heat evolution curve of cement hydration, the initial rapid hydration is followed by a dormant period, perhaps a couple of hours long, and the second heat generation, which is mainly due to additional hydration of C_3S , occurs at the end of the dormant period (37, 50). According to Verbeck (50), the initial setting time of cement paste lies somewhere between the end of the dormant period and the time when the maximum peak of the second heat generation is reached. Previte (29) obtained the same result.

Powers (5) has discussed the details of the processes he considered to be taking place up to the decline of the heat evolution rate after the second peak. This is the period in which we are interested from the standpoint of the setting process and the influence of retarders thereon.

The dormant period is thought to be due to a great diminution of the hydration reaction brought about by a coating of hydration products that limits the access of

water to the underlying anhydrous grains. For the C_3A the coating is presumably ettringite. For the C_3S , with which we are more concerned here, the coating is an initially-formed C-S-H gel. Powers (5) considered the reality of these ideas to be substantiated by various electron microscope studies of the appearance of the paste soon after mixing (52).

Powers considered the end of the dormant period and the beginning of the second heat evolution peak to be caused by a breakup of the coatings of hydration products that would allow an increase in the rate of hydration to take place. Indeed, if the dormant period is caused by such a coating, its removal, at least partially, is logically necessary for an increase in the hydration. The reason given for the breakup of the coating is the generation of an osmotic pressure by the concentration difference between the solutions outside the coating in the bulk aqueous phase and inside the coating adjacent to the anhydrous cement minerals.

In his recent review, Young (32) has classified the various possible modes of action of retarders into four categories. These are (i) adsorption, (ii) complexation, (iii) precipitation, and (iv) nucleation. The applicability of the results of the present study to these ideas will be discussed in reverse order.

One possible action is an influence on the nucleation of crystalline calcium hydroxide, changing the time at which macroscopic lime crystals are observed, which is about the same time as initial set. If this inhibition of crystallization and consequent supersaturation of lime in solution can inhibit further reaction of cement with water, then it may be important to the setting process. Young (32) considers this as perhaps the most important mode of action of retarders. It is well-known that small amounts of some dyes, surfactants, and other solutes can profoundly influence the habit and growth rate of crystalline phases (53). The most recent study of this effect in the phases of interest here is that of Berger and McGregor (54) who found that some of the substances studied here altered the crystal size and habit of the CH formed during C_3S hydration. They used, however, concentrations ten times those usually used in this study.

The only results developed here that apply directly to this aspect are those in which the four dyes were tested. These dyes were selected from the list of Buckley (53, p. 558) as being substances that strongly modify the habit of some growing crystals. They show some influence on the habit of CH grown slowly by interdiffusion of the ions (55). The change in the habit would have been caused by the effect that Young called "adsorption of organic compounds on the calcium hydroxide nuclei". But they show

negligible action as retarders. This is, of course, no proof that the substances that were strong retarders did not act in this way.

The precipitation idea is that retardation is brought about by some precipitation of, for example, the calcium salt of the retarder substance on the surface of the anhydrous grains. Young places no great importance on this idea. The applicability of this idea to the data of this study is referred to next in the discussion of complexation.

The complexation theory envisages the combination of the agent as some sort of complex, most likely with calcium or aluminum. It is true that many of the substances tested form complexes of greater or less stability with calcium or other metal ions. Furthermore, two of the substances that complex calcium strongly, ethylene diamine tetracetic acid (EDTA) and nitrilotriacetic acid (NTA) are fairly good retarders, although the larger dosage of EDTA did not result in as great an increase in retardation as was the case for the better retarders (Figure 15). Young (32) pointed out, there is no correlation between the stability constants of the calcium complexes of these substances and their potency as a retarder.

Any effect may even be in the opposite direction. The review of literature in Chapter II showed the retarders (lignosulfonate, sucrose, salicylic acid) generally

accelerated the very initial hydration of cement, but retarded subsequent hydration and transformations of some hydration products. The reason for the initial acceleration of cement hydration due to the addition of retarders has to be sought in some changes in ion concentration in the aqueous phase of cement paste. A few minutes after mixing cement with water, ions in the solution of cement paste would be saturated or supersaturated with respect to possibly each ion concentration. Any consumption of these ions would accelerate the hydration of the phases that can supply the ions into the solution. The consumption could be attained by any process such as precipitation or crystallization of hydration products, or complex formation of the ions with some chemicals.

It should be recalled that molecules of strong retarders contain many highly electronegative groups such as hydroxyl, acid, and carbonyl. These groups could complex metal ions in the aqueous phase of cement paste (13, 56). Whatever the states of the complexes, this complex formation would accelerate the hydration of cement paste, especially in the very early stages of the hydration, because more free organic molecules are available for complexing.

As a rough indication of the complexing ability of these materials under the conditions present in a cementitious system, the following test was performed. A

0.124M NaOH solution, which has an alkalinity equivalent to the aqueous phase of the usual cement paste, was prepared. In 100 ml of the solution, 0.2g of the retarder chemical was dissolved in a beaker. This gave a concentration in the solution equal to that in a 0.5 w/c paste. The solution was continuously stirred by a magnetic stirrer and was titrated with a 0.5M CaCl_2 solution until the first precipitate was detected. The result, volume of CaCl_2 solution necessary to give a precipitate, was plotted in Figure 51 against the relative initial setting time of the corresponding mortar specimen (w/c=0.50) in which the retarder has been added at a concentration of 0.1% of the cement.

In the blank test, the first precipitate of $\text{Ca}(\text{OH})_2$ was observed when the calcium chloride solution consumed was 0.9, 1.1, 0.9, 1.0, 0.8, 1.0, and 0.9 ml for several tests, the average being 0.94 ml. The chemicals that required more CaCl_2 solution for the titration than this blank amount must have complexed some calcium ions in the solution. The chemicals which show stronger complexing ability such as sucrose, gluconic acid, citric acid, and catchol would presumably induce more acceleration during the initial hydration of the cement, as mentioned earlier.

When some other chemicals were added, on the other hand, precipitates were observed earlier than in the case of the blank solution. These precipitates, presumably,

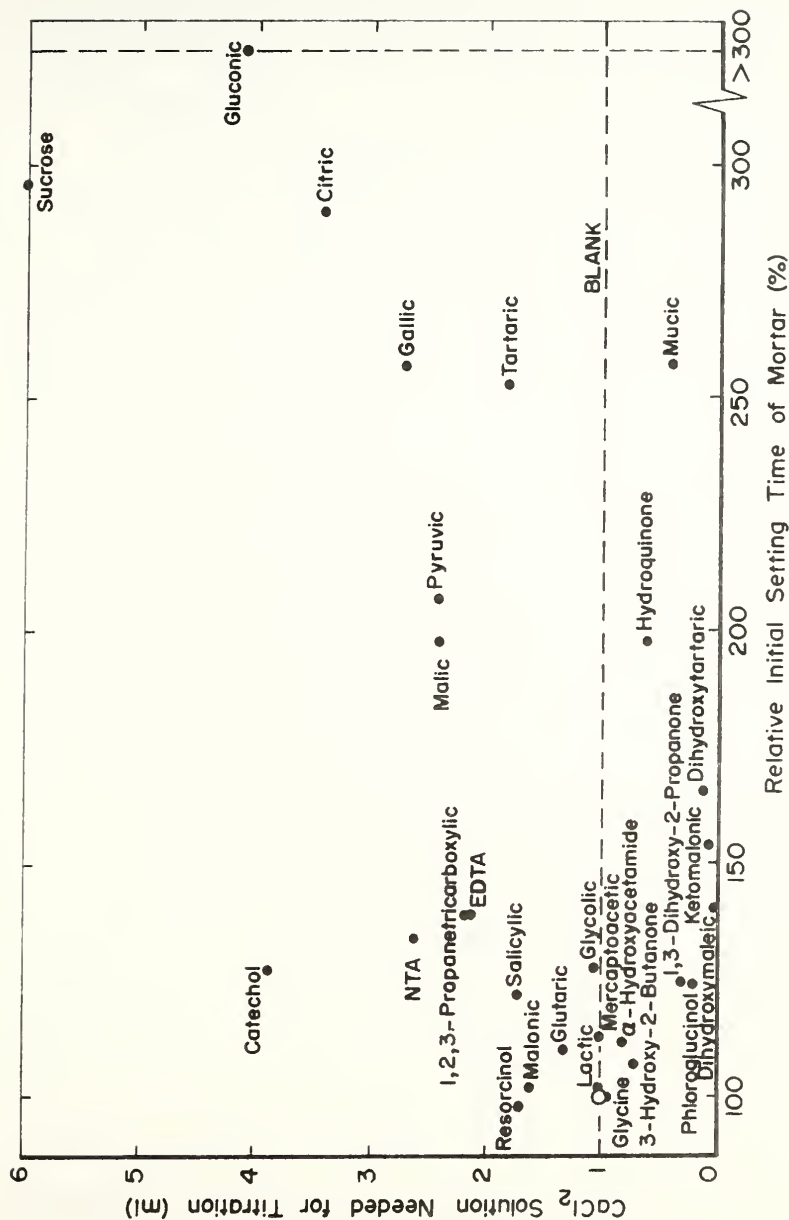


Figure 51 - Retarding Ability vs Complexing Ability of Chemicals

are not lime, but are insoluble calcium salts or complexes of these chemicals. Calcium lignosulfonate would fall in this category (19).

In any event, Figure 51 shows that many substances of strong "complexing" ability, as evidenced by the consumption of a relatively large amount of the CaCl_2 solution, are also strong retarders. But there are also many exceptions and the results are only qualitative. Also, as implied earlier in this section, any such agreement may be accidental if the main effect of complexation is to accelerate the very early reactions.

The discussion so far has emphasized the importance of the C_3S and has made little mention of the aluminates. In a cement that is normally-retarded with gypsum, the formation of ettringite acts to retard the otherwise too-rapid reaction of the C_3A . The aluminates, and especially the hydrated aluminates, have been shown to react with certain retarders to form adsorbed phases and/or complexes (7, 9, 14, 15). Such reactions may change the rate of consumption of various species, e.g. sulfate, and are important and complicated in their own right. But for the purposes here, it is considered that the main influence of the aluminates is to tie up more or less of the admixture in one way or another and so make less of it available to do whatever it does in connection with the silicate hydration process. The extent to which this

occurs with most of the retarders used in this study has not been investigated. It is, however, known that retarders would be more effective when used with cement of low C_3A (16, 17).

After and/or during the initial acceleration of cement hydration, retarders have to act in some way to retard subsequent cement hydration. Change in ion concentration in the aqueous phase of cement paste would probably not be concerned with the retardation mechanism any more. Hence, the mechanism has to be sought in direct interaction between remaining anhydrous cement grains or hydration products of cement and retarder molecules or complexes thereof. Additionally, the interaction must proceed in such a way that the effective molecular structures of retarders are most efficiently utilized for the retardation.

The adsorption, or "coating", theory was the earliest put forward to account for the influence of retarders on cement hydration. It was assumed that the retarder in some way became affixed to the cement grains and prevented their contact with the water in the same way that the ettringite on the C_3A and the calcium silicate hydrate on the silicates were presumed to act. This idea is consistent with the results of calorimetric experiments that showed retarders to extend the dormant period, i.e. delay the onset of the second heat evolution peak and spread it out over a longer time and with a smaller maximum value of heat

release rate (10, 16, 57). These results were for both portland cements and C_3S . Although the experiments were not extensive in terms of the admixtures used, they form the basis for the belief that, whatever else they may do, retarders delay set by delaying the chemical reactions between cement and water.

Several possible ways in which retarders might form such a coating or film have been suggested.

Hansen (11) suggested that the surfaces of C_3S (and C_3A) would be principally Ca^{++} or O^{--} ions, because these are larger and more numerous than ions of silicon and aluminum and, therefore, the latter would be screened by the former. Organic acids could presumably be attached by ionic attraction between Ca ions in the surface and the anionic carboxylate groups. Another suggested possibility (25) involves the fact that most retarder molecules contain hydroxyl groups, which are known to form hydrogen bonds with highly electronegative atoms such as oxygen atoms in the surfaces of the cement grains. Such bond could also be a mode of attachment of the retarder molecule.

Young (32) has also suggested that the attachment could be via some complex between surface atoms and the retarder molecules.

The work done by Blank et. al (7), however, showed that adsorption of retarders on C_3S from aqueous solution was negligible. Recently the same result was obtained with

more realistic concentrations of materials by Diamond (9). These results cast considerable doubt on any mechanism of retardation that involves adsorption of the agent on the anhydrous C_3S .

On the other hand Ramachandran (22) showed that it was hydrated C_3S , not C_3S , that was responsible for a perceptible amount of adsorption of calcium lignosulfonate from an aqueous solution. Diamond (9) obtained the same result with salicylic acid. The details of the surface structure of the C-S-H gel are unknown. Only speculation can be based on analogies with the structure of 11 \AA tobermorite (58) with which the gel is thought to have many similarities. It seems safe to say that the surface is probably composed of either oxygens or hydroxide groups and is partly covered with calcium ions abstracted from the solution phase that give it an overall net positive charge.

The formation of a discrete film of retarder molecules on the anhydrous minerals is conceivable. Indeed, the difficulty lies in the idea of too thick a film. If one assumes a concentration of retarder of 0.1% of the cement, a molecular weight of 100, and a coverage per molecule of 50 \AA^2 , then a cement with a fineness of $3000 \text{ cm}^2/\text{g}$ would have a layer of retarder ten molecules thick, which is unrealistic in light of the known processes of adsorption from solution.

If one considers the situation of adsorption on the hydrated phases, the results are more believable. Some dispute exists concerning the thickness of the hydrate layer covering the cement grains during the dormant period. Estimates range from several angstroms to several hundred (59). If one assumes 5% of the cement is hydrated during, or at the end of, the dormant period, and if the specific surface of the hydrated product is $200 \text{ m}^2/\text{g}$, then the retarder would be sorbed on only 25% of this material.

It was found in this work that the chemicals effective as retarder have molecular configurations in which most of the hydrogen atoms around a molecule are strongly polarized by many electronegative groups. Stronger polarization of hydrogen atoms would lead to stronger adsorption on charged surfaces of the hydration products of cement. More numerous polarized hydrogen atoms would result in more efficient coverage of the molecules on the hydration products.

Further, the most efficient retarders have several, and usually many, oxygens closely grouped and so constrained either by frequency along the chain or rigidity of a ring structure. These oxygens can be in hydroxyl, carbonyl, or carboxyl groups. These groups can participate in bonding to surfaces of the hydration products by hydrogen bonding to surface oxygens in the solid hydrate or by ionic attraction to calcium sorbed on the surfaces. A close grouping as well as a large number of such groups in the

retarder molecule would presumably lead to stronger bonding of the molecule to the solid.

The questions still remains of the mode of action of retarders. Assuming, as seems likely, that they are sorbed out of solution onto the initially-formed C-S-H gel, how do they thereby delay the hydration and set?

In view of the probability of less than a monolayer being formed on the solid hydrate surfaces, it seems unlikely that the sorbed molecules act as a physical barrier to the passage of water inward to the unreacted minerals. There could, of course, be some kind of partial "plugging" action that could retard the passage of some water, especially since the good retarders have a highly oxygenated structure that could exert some binding influence on adjacent water molecules by hydrogen bonding and thus generate an effectively larger structure with a better blocking action.

Another possibility may be more likely. At least it satisfies the known facts. As previously mentioned, if the dormant period is caused by a "coating" of C-S-H gel on the silicate surfaces (the aluminates being controlled by the gypsum), then this coating must partially break up for increased reaction to occur and bring about the onset of the second heat peak. Whatever the force impelling the breakup of the coating, if the coating is mechanically stronger it would resist the breakup longer, and when it

occurred it would be less extensive and result in a "milder" second heat peak. Such a result would be consistent with the observed calorimetric data. So it is postulated that the retarder molecules sorb on the initially formed hydrate material and that some of the molecules will sorb in areas where the gel particles are already in close contact and are coherent. The molecular structure of good retarders is such that they have regions (the highly oxygenated or charged parts of the molecule) that can sorb over a large part of the molecule and that presumably do so relatively strongly. If they sorbed onto two adjacent gel particles the resulting bonding would, according to elementary calculations, result in a considerable increase in the resistance to rupture by whatever forces ultimately break up the coating. No doubt many of the molecules would sorb on only the surface of one particle of gel, but some of the pore spaces are so small, even in a mature gel, that it is reasonable to envisage such a bridging action of the retarder molecule and a consequent increase in the mechanical strength of the coating. It is recognized that this is only a postulate, which requires much more work to establish or refute, but at least it fits most of the known facts.

From the discussion of the retardation mechanisms above, it appears that strong retarders not only accelerate the initial hydration of cement by removing possibly more

calcium ions or other metal ions from the aqueous phase of cement paste, but also have molecular configurations that can either cover or bridge the hydration products on cement grains more efficiently. Even if a chemical has an apparently effective molecular structure, it may not act as strongly as expected unless it can accelerate the initial cement hydration and unless the molecular adsorption on the hydration products on cement grains proceeds efficiently. Examples may be mucic, dihydroxytartaric or dihydroxymaleic, and ketomalonic acids that are considerably weaker retarders than gluconic, tartaric, and tartronic acids, correspondingly, regardless of their similar molecular structures. These are the chemicals that seem to have precipitated when only little CaCl_2 was added in alkaline solution (Figure 51). Either only a little complex formation or less efficient action for adsorption would be expected for these chemicals.

Effect of Retarders on the Shrinkage of Cement Pastes

As shown in Figures 16 and 17, the addition of retarders altered the shrinkage of cement paste significantly at earlier ages and increased the shrinkage to some extent at later ages, when the samples were dried in the vacuum oven for 24 hours. However, the general trend of the relation between degree of cement hydration and shrinkage was the same for all the samples. An early peak of shrinkage occurred at about 25% hydration of the cement, and then the

shrinkage decreased to a minimum of 0.7-0.8% at about 60% hydration. Thereafter the shrinkage increased parabolically as the paste became more mature.

It would be normally expected that a longer period of cement hydration would induce larger shrinkage of cement paste, because larger amounts of C-S-H gel, which is the component causing the shrinkage, are produced. The increased shrinkage can be also explained by the reduction of the amount of unhydrated cement grains, which act as a "microaggregate" and restrain the shrinkage of the cement gel (60). The latter idea is similar to the shrinkage-restraining action of aggregates in concrete (61).

However, these ideas do not explain the existence of the first peak observed in most of the shrinkage curves. Part of the effect could be due to the slightly greater "efficiency" with which the young and immature pastes were dried by being in the vacuum oven for a constant time of 24 hours. The pastes continued to lose a little water and to shrink appreciably when they were kept in the oven for longer times; this effect was greater for the more mature pastes (Figures 52 and 53). Also, the less mature pastes probably had a considerably lower elastic modulus than the more mature ones, an effect that would result in greater deformations for a given driving force of shrinkage. It should be noted here that the data points were closely grouped about the curves and that the effects being

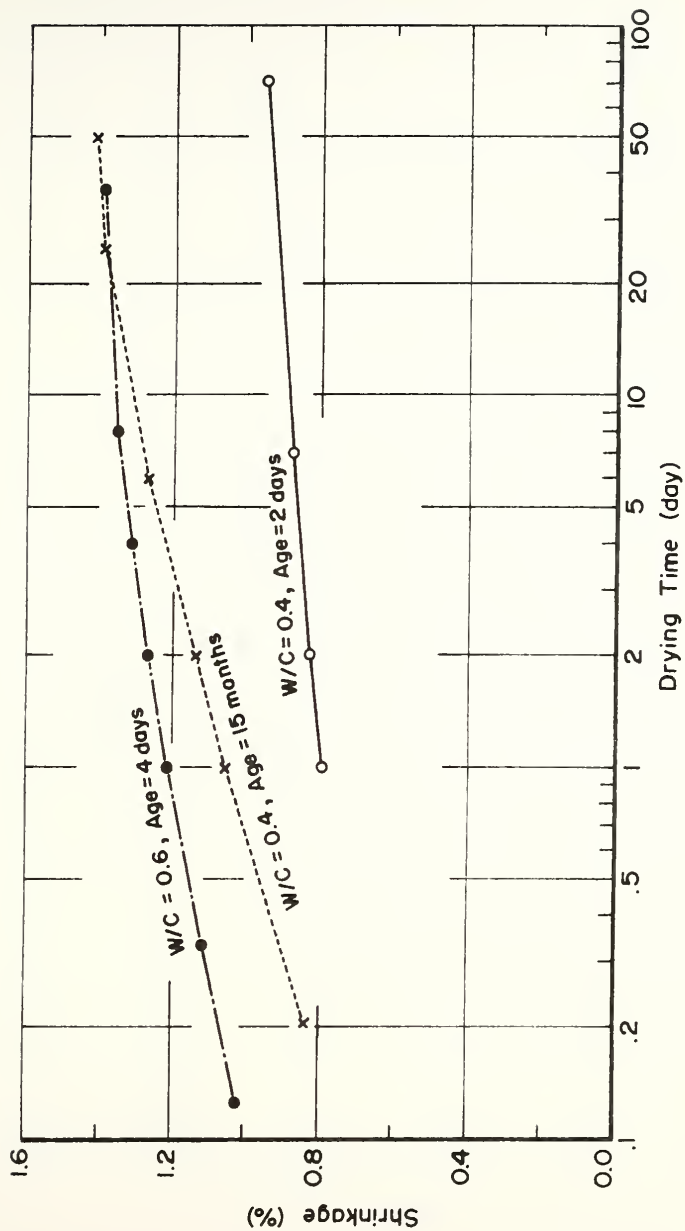


Figure 52 - Effect of Continuous Vacuum Oven-Drying on Shrinkage of Cement Pastes

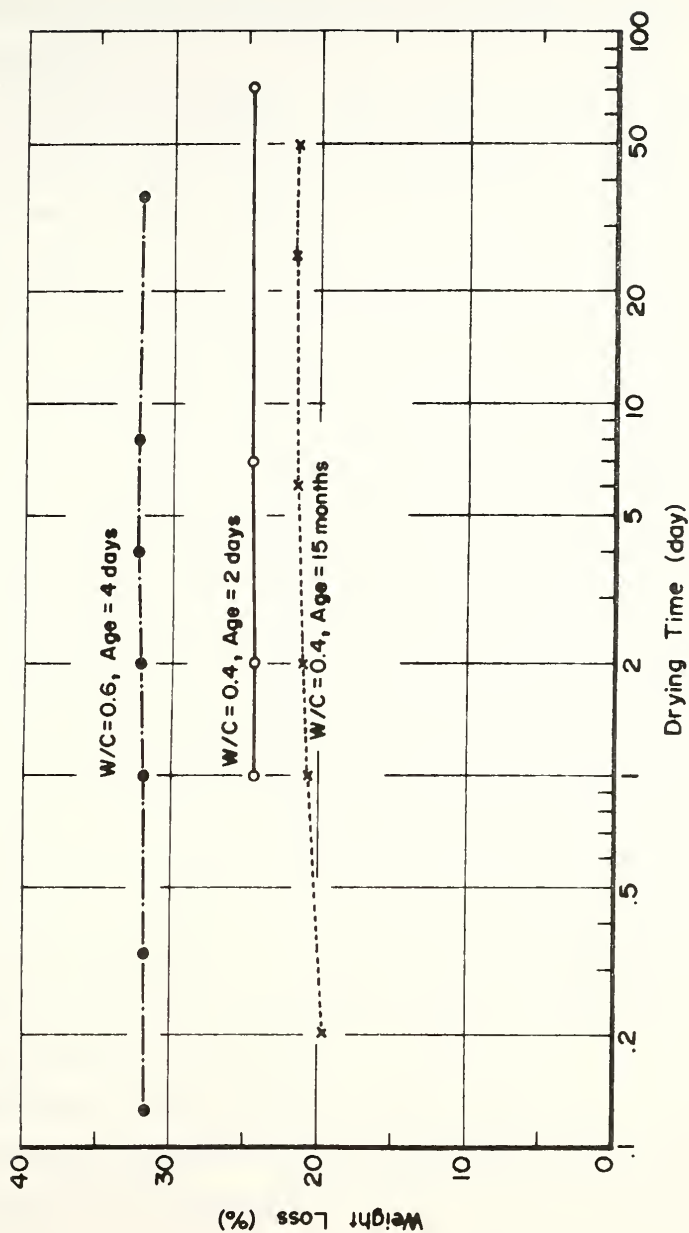


Figure 53 - Effect of Continuous Vacuum Oven-Drying on Weight Loss of Cement Pastes

described are real, rather than the result of experimental variability.

According to Powers (62), menisci in which hydrostatic tension develops can not form at humidities below about 45%, and all the evaporable water in cement paste at 45% R.H. exists as adsorbed water on the solid phases. In explaining the shrinkage of cement pastes at humidities below the vapor pressure at which menisci vanish, Mills (63) ascribed the shrinkage to the reduction of swelling pressure in gel water which is adsorbed on the cement gel. Verbeck and Helmuth (35), on the other hand, said that water held by cement paste below 30% R.H. is not "adsorbed water" but rather is in a state similar to that of inter-layer water in clays. So there is some question about the exact state of the water in pastes at relatively low humidities. However, it is known that only those water molecules that are held tightly by the solid phase are left when the paste is severely dried. Therefore, the measured shrinkage should be directly related to the properties of the solid phases, and especially of the hydration products. Since the amount of unhydrated cement is constant at a certain degree of hydration, it appears that the observed difference in shrinkage due to the addition of retarders has to be attributed to some modification of the properties of the hydration products.

According to other workers, retarders do not alter the composition or identity of the hydration products, but change only the rate of cement hydration (1, 8). The scanning electron microscope did not show any noticeable difference among the hydration products of cement pastes with and without retarders after more than 20% of the cement hydrated. Therefore, the only conceivable modifications by retarders would be either some morphological changes in the microstructure of the hydration products or a difference in the relative amounts of hydration products produced from each compound of cement, or both. Whatever the reason is, specific surface area measurement on the hydration products should reveal some of the evidence, because the shrinkage would have been caused by removal of water molecules from their surfaces.

As shown in Figures 28, 29, and 30, the retarders, in fact, changed the specific surface areas of the hydration products, and the change was frequently closely related to the shrinkage behavior of corresponding cement paste. For example, those retarders which induced the larger shrinkage at earlier ages increased the specific surface area at the ages and the subsequent change was also similar to that in shrinkage. The consistently larger shrinkage of the cement paste with calcium chloride would be well explained by the consistently larger specific surface area of the hydration products.

It is of interest to note that for the control paste with no admixture the minimum in the shrinkage curve coincided well with that in the surface area development curve, at about 60% hydration. The maximum, however, occurred somewhat earlier for the shrinkage curve, at 25% as opposed to 45% for the surface area. They would not, of course, be expected to be exactly similar, because of changing secondary affects, such as the elastic modulus.

For the commercial retarders, it may be significant that at later ages all admixtures gave pastes of slightly higher shrinkages than the control, whereas all except S gave slightly smaller areas. For the pure chemicals the relationship is equally mixed. At intermediate maturities of the paste, near the minimum shrinkage, many of the pure compounds resulted in significantly larger specific surfaces, while causing only a small increase in the shrinkage.

For the younger pastes, one would expect a closer correspondence between shrinkage and specific surface because their structures are less influenced by later, secondary, processes. This seems to be the case for A and S, although L gave a somewhat higher surface, but slightly smaller shrinkage. All the pure chemical gave pastes of higher surface area in the immature pastes, and all also gave higher shrinkage except 3-hydroxy-2-butanone and hydroquinone. It may be significant (Figure 25) that hydroquinone seems to

have been atypical in that it did not slow down the hydration rate, as determined by W_n , but did retard the set. When the sample bars were demolded, the one containing hydroquinone seemed to have a hardened core and a still-soft exterior. The reasons for this anomalous behavior are not known. The unusual shape of the curve for sucrose should also be noted.

In all matters involving the specific surface area, it should be remembered that different batches of samples hydrate somewhat differently, even though the mixing and curing conditions were as similar as possible. The data for the control pastes were obtained from five different batches, and they show such a variability. Therefore caution should be observed in drawing conclusions from small variations in this parameter.

In general, however, at the younger ages the shrinkage behavior changes in a manner similar to the specific surface, which is logical.

It should be recalled, that the adsorption process of retarder molecules is not necessarily the same for all the retarders. Such differences may have caused kinetic changes in the subsequent hydration of each cement compound in these samples.

Retarders also increased the shrinkage of mature cement pastes (10 months old) when the samples were dried at 50% R.H. (Figure 18 and 19). Menisci can exist in small pores

of the pastes in this case, and the drying would be equivalent to a severe condition for normal concrete members in the field. In interpreting these kinds of shrinkage data, however, one can not forget that the delayed hydration of cement due to the addition of retarders normally recovers in 2 to 3 days, and retarders rather accelerate the subsequent hydration (see Figures 24 and 25). Then, it would be apparent from the previous discussion that, if the comparison is made at an equal age, retarders generally increase the shrinkage of older cement paste. The comparison at an equal age would have a practical meaning. But the result may not be necessarily caused by the modified property of hydration products by retarders but could be caused simply by the difference in the degree of cement hydration.

The relationships between shrinkage and weight loss of the same samples revealed that the relation was more or less the same as that of the control sample for all of the samples except for the sample with retarder S. Hence, it can be said that the observed increase in the shrinkage of the samples are mostly caused by the difference in the degree of cement hydration, for drying at 50% R.H.

Although the determination of evaporable water content of cement paste was made carefully as possible, the results scattered in a relatively wide range, and no information was obtained as to why only retarder S increased

the shrinkage. It should be recalled that retarder S increased the specific surface area of the hydration products remarkably at later stage of the hydration. Presumably, the effect of this increased specific surface area would have remained even at the intermediate humidity. This would, in turn, indicate a possibility that the modified property of hydration products by retarders may affect the shrinkage of cement paste in a relatively severe drying condition.

CONCLUSIONS

The following conclusions seem reasonable. They are based on the materials used and the tests performed.

1. Strong retarders have a molecular composition that includes many oxygen atoms constrained to approach each other closely. Hydroxyl, carboxyl, and carbonyl are all effective, and carbonyl seems especially strong in its influence. Many α -hydroxy acids are retarders, but the presence of other groups can exert a strong effect reducing the retarding action. The oxygen-containing groups can be presumed to exert polarizing influences that could contribute to relatively strong adsorption onto the solid surfaces of concern.

2. More weakly electronegative atoms on the molecule do not have the same effect as oxygens.

3. When cement pastes are strongly dried of all their evaporable water, they exhibit shrinkage behavior that shows a minimum at about half hydration and an earlier maximum. This behavior is also exhibited by the change in specific surface area of the hydrated cement; the hydrate gains appreciable surface area between about 60% and 80% hydration, and thereafter remains relatively unchanged.

Some cause and effect relationship exists between the specific surface area of a paste and its shrinkage potential, although other factors, such as restraint by unhydrated cement, are probably also operative.

4. Retarders cause a moderate increase in the shrinkage of cement pastes at ages greater than about half hydration. At lesser ages the shrinkage may be either increased or decreased.

5. The changes in shrinkage brought about by retarders can be partially ascribed to those brought about in specific surface areas of the hydrated cement, but other effects, probably related to the chemical species present, are also important.

LIST OF REFERENCES

LIST OF REFERENCES

- (1) M. E. Prior, and A. B. Adams, "Introduction to Producers' Papers on Water-Reducing Admixtures and Set-Retarding Admixtures for Concrete" ASTM STP No. 266, 1960, pp. 171-179.
- (2) R. C. Mielenz, "Water-Reducing Admixtures and Set-Controlling Admixtures for Concrete: Uses; Specifications; Research Objectives" ASTM STP No. 266, 1960, pp. 218-233.
- (3) G. B. Wallace and E. L. Ore, "Structural and Lean Mass Concrete as Affected by Water-Reducing, Set-Retarding Agents" ASTM STP No. 266, pp. 38-94.
- (4) B. Tremper and D. L. Spellman, "Shrinkage of Concrete - Comparison of Laboratory and Field Performance" Highway Research Record, Pub. 1067, No. 3, 1963, pp. 30-61.
- (5) T. C. Powers, "Some Physical Aspects of the Hydration of Portland Cement" Journal of the PCA Research and Development Laboratories, No. 3, Vol. 1, Jan. 1961, pp. 47-56.
- (6) J. F. Young, "Hydration of Tricalcium Aluminate with Lignosulfonate Additives" Magazine of Concrete Research, Vol. 14, No. 42, Nov. 1962, pp. 137-142.
- (7) B. Blank, D. R. Rossington, and L. A. Weinland, "Adsorption of Admixtures on Portland Cement" Journal of the American Ceramic Society, Vol. 46, No. 8, Aug. 1963, pp. 395-399.
- (8) P. Seligmann and N. R. Greening, "Studies of Early Hydration Reactions of Portland Cement by X-Ray Diffraction" Highway Research Record, No. 62, 1964, pp. 80-105.

- (9) S. Diamond, "Interactions Between Cement Minerals and Hydroxycarboxylic-Acid Retarders: I, Apparent Adsorption of Salicylic Acid on Cement and Hydrated Cement Compound" Journal of the American Ceramic Society, Vol. 54, No. 6, June 1971, pp. 273-276.
- (10) H. N. Stein, "Influence of Some Additives on the Hydration Reactions of Portland Cement II. Electrolytes" Journal of Applied Chemistry, Vol. II, Dec. 1961, pp. 482-492.
- (11) W. C. Hansen, "Action of Calcium Sulfate and Admixtures in Portland Cement Paste" ASTM STP No. 266, 1960, pp. 3-25 and 36-37.
- (12) R. C. Mielenz and R. B. Peppler, Discussion of the paper by W. C. Hansen, ASTM STP No. 266, 1960, pp. 35-36.
- (13) K. E. Daugherty and M. J. Kawalewski, Jr., "Effect of Organic Compounds on the Hydration Reactions of Tricalcium Aluminate" Proceedings of the Fifth International Symposium on the Chemistry of Cement, Tokyo, 1968, Vol. IV, pp. 42-51.
- (14) S. Diamond, "Interactions Between Cement Minerals and Hydroxycarboxylic-Acid Retarders: II, Tricalcium Aluminate-Salicylic Acid Reaction" Journal of the American Ceramic Society, Vol. 55, No. 4, April 1972, pp. 177-180.
- (15) S. Diamond, "Interactions Between Cement Minerals and Hydroxycarboxylic-Acid Retarders: III, Infrared Spectral Identification of the Aluminosalicylate Complex" Journal of the American Ceramic Society, Vol. 55, No. 8, Aug. 1972, pp. 405-408.
- (16) L. R. Forbrich, "The Effect of Various Reagents on the Heat Liberation Characteristics of Portland Cement" Proceedings of the American Concrete Institute, Vol. 37, Nov. 1940, pp. 161-181.
- (17) M. Polivak and A. Klein, "Effect of Water-Reducing Admixtures and Set-Retarding Admixtures as Influenced by Portland Cement Composition" ASTM STP No. 266, 1960, pp. 124-139.
- (18) G. M. Bruere, "Importance of Mixing Sequence When Using Set-Retarding Agents with Portland Cement" Nature, Vol. 199, July 1963, pp. 32-33.

- (19) V. H. Dodson and E. Farkas, "Delayed Addition of Set Retarding Admixtures to Portland Cement Concrete" Proceedings, ASTM 64, 1962.
- (20) G. L. Kalousek, C. H. Jumper, and J. J. Tregoning, "Composition and Physical Properties of Aqueous Extracts From Portland Cement Clinker Paste Containing Added Materials" Journal of Research of the National Bureau of Standards, Vol. 30, March 1943, pp. 215-255.
- (21) F. C. Tamas, "Acceleration and Retardation of Portland Cement Hydration by Additives" Highway Research Board, Special Report 90, 1966, pp. 392-397.
- (22) V. S. Ramachandran, "Interaction of Calcium Ligno-sulfonate with Tricalcium Silicate, Hydrated Tricalcium Silicate, and Calcium Hydroxide" Cement and Concrete Research, Vol. 2, 1972, pp. 179-194.
- (23) H. H. Steinour, Discussion of the paper by W. C. Hansen, ASTM STP No. 266, 1960, pp. 25-33.
- (24) W. C. Hansen, "Oil Well Cements" Proceedings of the Third International Symposium on the Chemistry of Cement, London, Cement and Concrete Association, 1952, pp. 598-627.
- (25) H. H. Steinour, Discussion of the paper by W. C. Hansen, Proceedings of the Third International Symposium on the Chemistry of Cement, London, Cement and Concrete Association, 1952, pp. 627-631.
- (26) H. H. Steinour, "The Setting of Portland Cement" A Review of Theory, Performance and Control, Research Department Bulletin 98, PCA, 1958.
- (27) J. H. Taplin, Discussion of the paper by H. E. Vivian, Proceedings of the Fourth International Symposium on Chemistry of Cement, National Bureau of Standards, Monograph 43-II, 1960, pp. 924-925.
- (28) U. Danielson, "Studies of the Effect of Simple Organic Admixtures on the Properties of Cement Paste" International Symposium on Admixtures for Mortar and Concrete, Burssels, Aug.-Sept., 1967, pp. 59-68.
- (29) R. W. Previte, "Some Insight on the Mechanism of Saccharide Set Retardation of Portland Cement" Cement and Concrete Research, Vol. 1, 1971, pp. 301-316.

- (30) G. M. Bruere, "Set-Retarding Effects of Sugars in Portland Cement Pastes" *Nature*, Vol. 212, Oct. 1966, pp. 502-503.
- (31) S. Koide, Discussion of the paper by K. E. Daugherty and M. J. Kawalewski Jr., *Proceedings of the Fifth International Symposium on the Chemistry of Cement*, Tokyo, 1968, Vol. IV, p. 52.
- (32) J. F. Young, "A Review of the Mechanisms of Set-Retardation in Portland Cement Pastes Containing Organic Admixtures" *Cement and Concrete Research*, Vol. 2, 1972, pp. 415-433.
- (33) R. C. Mielenz, "Use of Surface-Active Agents in Concrete" *Proceedings of the Fifth International Symposium on the Chemistry of Cement*, Tokyo, 1968, Vol. IV, pp. 1-29.
- (34) A. M. Neville, "Hardened Concrete: Physical and Mechanical Aspects" *American Concrete Institute Monograph*, No. 6, 1971, pp. 119-141.
- (35) G. J. Verbeck and Helmuth, "Structures and Physical Properties of Cement Paste" *Proceedings of the Fifth International Symposium on the Chemistry of Cement*, Tokyo, 1968, Vol. III, pp. 1-32.
- (36) B. Tremper, Discussion of the paper by G. B. Wallace and E. L. Ore, *ASTM STP No. 266*, 1960, pp. 94-96.
- (37) W. Lerch, "The Influence of Gypsum on the Hydration and Properties of Portland Cement Pastes" *Research Department Bulletin 12*, PCA, March 1946.
- (38) H. E. Schwiete, U. Ludwig, and K. Seiler, "Die Wirkungsweise von Erstarrungsverzögerern unter besonderer Berücksichtigung silikofluorhaltiger Verzögerer" *Institut für Gesteinshüttenkunde*, 1969.
- (39) J. Okabe, K. Nakajima, and T. Yoshihara, "Investigations on the Method of Test for Setting Time of Concrete Containing Water Reducing Admixture" *Proceedings of the Fifth International Symposium on the Chemistry of Cement*, Tokyo, 1968, Vol. IV, pp. 58-64.
- (40) H. S. Washington, "The Chemical Analysis of Rocks" *John Wiley & Sons, Inc.*, 1930, pp. 242-245.
- (41) P. G. Jeffery, "Chemical Methods of Rock Analysis" *Pergamon Press*, 1970, pp. 169-170 (Method of Shapiro and Brannock).

- (42) R. F. Feldman and P. J. Sereda, "A Model for Hydrated Portland Cement Paste as Deduced from Sorption-Length Change and Mechanical Properties" *Materiaux et Constructions*, Vol. 1, No. 6, 1968, pp. 509-520.
- (43) R. F. Feldman, "The Flow of Helium into the Interlayer Spaces of Hydrated Portland Cement Paste" *Cement and Concrete Research*, Vol. 1, No. 3, May 1971, pp. 285-300.
- (44) S. Brunauer, I. Odler, and M. Yudenfreund, "The New Model of Hardened Portland Cement Paste" *Highway Research Record*, No. 328, 1970, pp. 89-107.
- (45) R. F. Feldman, "Assessment of Experimental Evidence for Models of Hydrated Portland Cement" *Highway Research Record*, No. 370, 1971, pp. 8-24.
- (46) S. J. Gregg and K. S. W. Sing, "Adsorption, Surface Area, and Porosity" Academic Press, 1967, pp. 36-41.
- (47) T. C. Powers and T. L. Brownyard, "Studies of the Physical Properties of Hardened Portland Cement Paste" *Research Department Bulletin 22, PCA*, March 1948, pp. 469-504.
- (48) W. J. Halstead and B. Chaiken, "Water-Reducing Retarders for Concrete - Chemical and Spectral Analyses" *Highway Research Board Bulletin 310*, 1962, pp. 33-55.
- (49) W. E. Grieb, G. Werner, and D. O. Wolf, "Tests of Retarding Admixtures for Concrete" *Highway Research Board Bulletin 310*, 1962, pp. 1-32.
- (50) G. Verbeck, "Cement Hydration Reactions at Early Ages" *Research Department Bulletin 189, PAC*.
- (51) H. E. Schwiete, U. Ludwig, and P. Jäger, "Investigations in the System $3\text{CaO} \cdot \text{Al}_2\text{O}_3 - \text{CaSO}_4 - \text{CaO} - \text{H}_2\text{O}$ " *Highway Research Board, Special Report 90*, 1966, pp. 353-367.
- (52) L. E. Copeland and E. G. Schulz, Discussion to the paper by Ake Grudemo, *Proceedings of the Forth International Symposium on Chemistry of Cement*, Washington, 1960, Vol. II, pp. 648-655.
- (53) H. E. Buckley, "Crystal Growth" John Wiley & Sons Inc., 1951, p. 571.

- (54) R. L. Berger and J. D. McGregor, "Influence of Admixtures on the Morphology of Calcium Hydroxide Formed During Tricalcium Silicate Hydration" *Cement and Concrete Research*, Vol. 2, No. 1, 1972, pp. 43-55.
- (55) W. L. Dolch, Private Communication.
- (56) L. L. Alt, "Spectrophotometric Determination of Gluconic Acid and Its Salts" *Analytical Chemistry*, Vol. 27, No. 5, May 1955, pp. 749-751.
- (57) H. N. Stein, "Influence of Some Additives on the Hydration Reactions of Portland Cement I. Non-Ionic Organic Additives" *Journal of Applied Chemistry*, Vol. 11, Dec. 1961, pp. 474-482.
- (58) H. F. W. Taylor, "The Chemistry of Cement", Vol. I, Academic Press, 1964, pp. 187-189.
- (59) K. Fujii and W. Kondo, "Hydration of Tricalcium Silicate in a Very Early Stage" *Proceedings of Fifth International Symposium on the Chemistry of Cement*, Tokyo, 1968, Vol. II, pp. 362-371.
- (60) G. Verbeck, "Shrinkage of Concrete - Applied Research Studies" *PCA Annual Meeting*, 1961.
- (61) G. Pickett, "Effect of Aggregate on Shrinkage of Concrete and Hypothesis Concerning Shrinkage" *Proceedings of the American Concrete Institute*, Vol. 52, No. 5, Jan. 1956, pp. 581-590.
- (62) T. C. Powers, "Physical Properties of Cement Paste" *Research Department Bulletin 154*, PCA.
- (63) R. H. Mills, "Effects of Sorbed Water on Dimensions, Compressive Strength and Swelling Pressure of Hardened Cement Paste" *Highway Research Board*, Special Report 90, 1966, pp. 84-111.

APPENDICES

APPENDIX A

APPENDIX A

Correction Curve for Warping of Cement Paste Bars

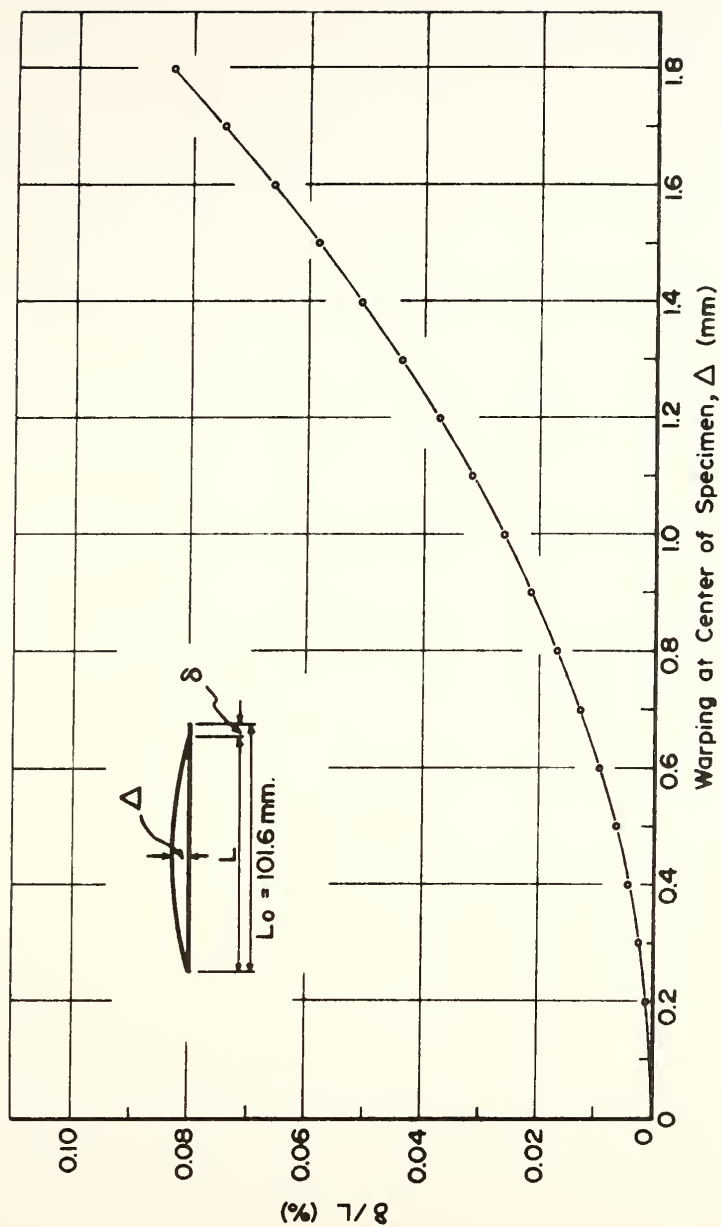


Figure 54 - Correction Curve for Warping of Cement Paste Bars

APPENDIX B

APPENDIX B

Summary of Setting Time Experiments When
Pure Chemicals were Added

Setting times are expressed in terms of T50, T100, T500, and T4000 which are the relative retardations at the penetration resistances of 50, 100, 500 and 4000 psi, respectively, to the retardation of plain mortar with no admixture.

Table 7 - Summary of Relative Setting Time of Mortar Samples When Pure Chemicals Were Added

concentration: 0.1% of cement

Chemical	Setting Time (%)			
	T50	T100	T500	T4000
Malonic Acid	110	107	102	97
Succinic Acid	105	109	110	112
Glutaric Acid	110	110	110	106
Adipic Acid	104	100	101	105
Glycolic Acid	136	129	128	121
Glycine	100	100	100	106
Mercaptoacetic Acid	113	112	113	106
Glyoxylic Acid (Hydrate)	122	125	127	126
Pyruvic Acid	195	206	207	185
Lactic Acid	102	100	102	100
α -Hydroxy-N-Butyric Acid	98	100	100	101
Ketomalonic Acid (Disodium)	153	159	154	153
Tartronic Acid	120	183	278	*
(-) Malic Acid	196	203	198	174
d-Tartaric Acid	200	249	254	212
Dihydroxymaleic Acid	134	145	141	135
Dihydroxytartaric Acid	140	165	166	155

* Retardation is too large to determine in the limit of the experiment.

Table 7, cont.

Chemical	Setting Time (%)			
	T50	T100	T500	T4000
3-Hydroxypropionic Acid	100	100	102	104
Mucic Acid	207	255	257	*
Gluconic Acid	146	270	>300	*
2-Ketoglutaric Acid	211	261	292	*
1,2,3-Propanetricarboxylic Acid	141	139	139	137
Citric Acid	200	287	286	*
Crotonic Acid	104	103	101	102
Acetaldol	106	105	103	105
Methyl Glycolate	102	108	113	109
α -Hydroxyacetamide	108	108	112	110
1,3-Dihydroxy-2-Propanone	120	129	125	115
3-Hydroxy-2-Butanone	114	112	107	107
N-Methylpropionamide	113	111	109	109
Ethyl Acetoacetate	121	115	107	113
Allyl Alcohol	104	100	100	111
2-Butene-1,4-Diol	100	100	100	100
2,4-Pentanedione	118	120	108	113
Pentaerythritol	98	100	102	100
Sucrose	218	256	>300	*
Resorcinol	107	95	98	96

Table 7, cont.

Chemical	Setting Time (%)			
	T50	T100	T500	T4000
Catechol	111	124	127	123
Hydroquinone	215	196	198	172
m-Nitrophenol	109	108	107	106
o-Nitrophenol	109	109	109	106
p-Nitrophenol	101	102	102	102
m-Hydroxybenzoic Acid	103	102	103	103
Salicylic Acid	127	123	122	122
p-Hydroxybenzoic Acid	98	98	102	98
Benzoic Acid	105	103	103	106
Benzyl Alcohol	104	103	101	105
DL-Mandelic Acid	100	102	107	106
o-Hydroxyacetophenone	103	105	108	110
Pictric Acid	113	112	117	118
Pyrogallol	204	219	239	188
Phloroglucinol	123	129	131	129
Gallic Acid	238	219	257	*
2,4,6-Trihydroxybenzoic Acid	167	207	217	186
EDTA	136	136	139	131
Nitrilotriacetic Acid	144	149	134	132

Table 7, cont.

Chemical	Setting Time (%)			
	T50	T100	T500	T4000
Dye 27195 (282)	97	100	100	99
Dye 25380 (353)	92	93	96	94
Dye 24410 (518)	113	121	110	112
Dye 42755 (707)	104	100	102	99
Eriochrome Black T	105	104	103	101
Calcium Lignosulfonate	123	125	118	126

continued

Table 7, cont.

Chemical	concentration: 0.5% of cement			
	Setting Time (%)			
	T50	T100	T500	T4000
Malonic Acid	162	155	145	143
Succinic Acid	122	129	137	135
Glutaric Acid	103	100	100	99
Glycolic Acid	182	446	*	*
Glycine	99	98	96	92
Mercaptoacetic Acid	141	136	128	121
Monochloroacetic Acid	105	113	108	110
Lactic Acid	123	122	118	115
Glycerine	96	94	92	92
Acetaldo1	100	97	93	92
Methyl Glycolate	262	323	315	*
α -Hydroxyacetamide	286	349	*	*
1,3-Dihydroxy-2-Propanone	47	48	97	197
3-Hydroxy-2-Butanone	190	184	173	158
Ethyl Acetoacetate	175	176	177	170
2-Butene-1,4-Diol	109	104	102	104
Chloral Hydrate	105	102	104	107
Pictric Acid	107	109	112	116
EDTA	166	177	184	173

APPENDIX C

APPENDIX C

Shrinkage of Vacuum Oven-Dried Cement Pastes
at Various Stages of Cement Hydration

The following abbreviations are used in this part.

h: hour(s)

d: day(s)

m: month(s)

Each data point is the average of two separate measurements. The range of duplicate measurements was usually about 1% of the average.

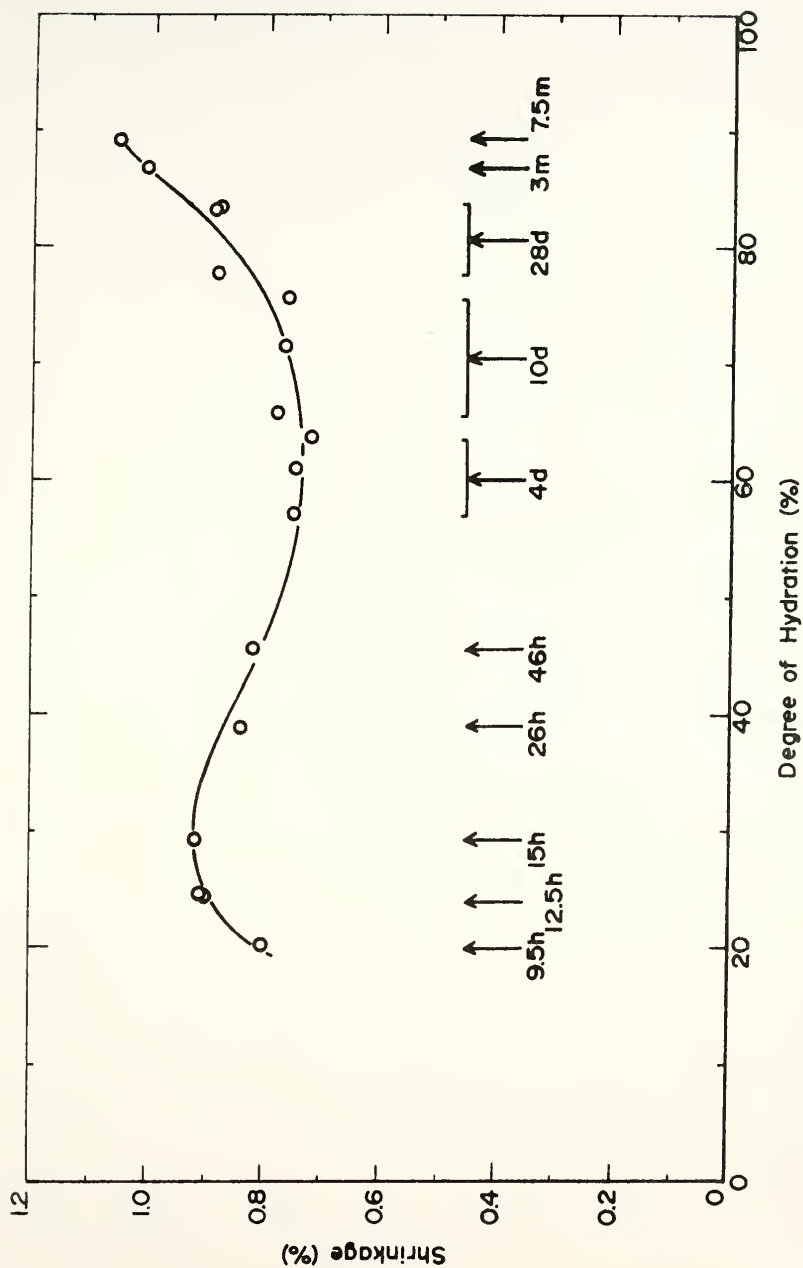


Figure 55 - Shrinkage of Vacuum Oven-Dried Cement Pastes at Various Stages of Cement Hydration (No Admixture)

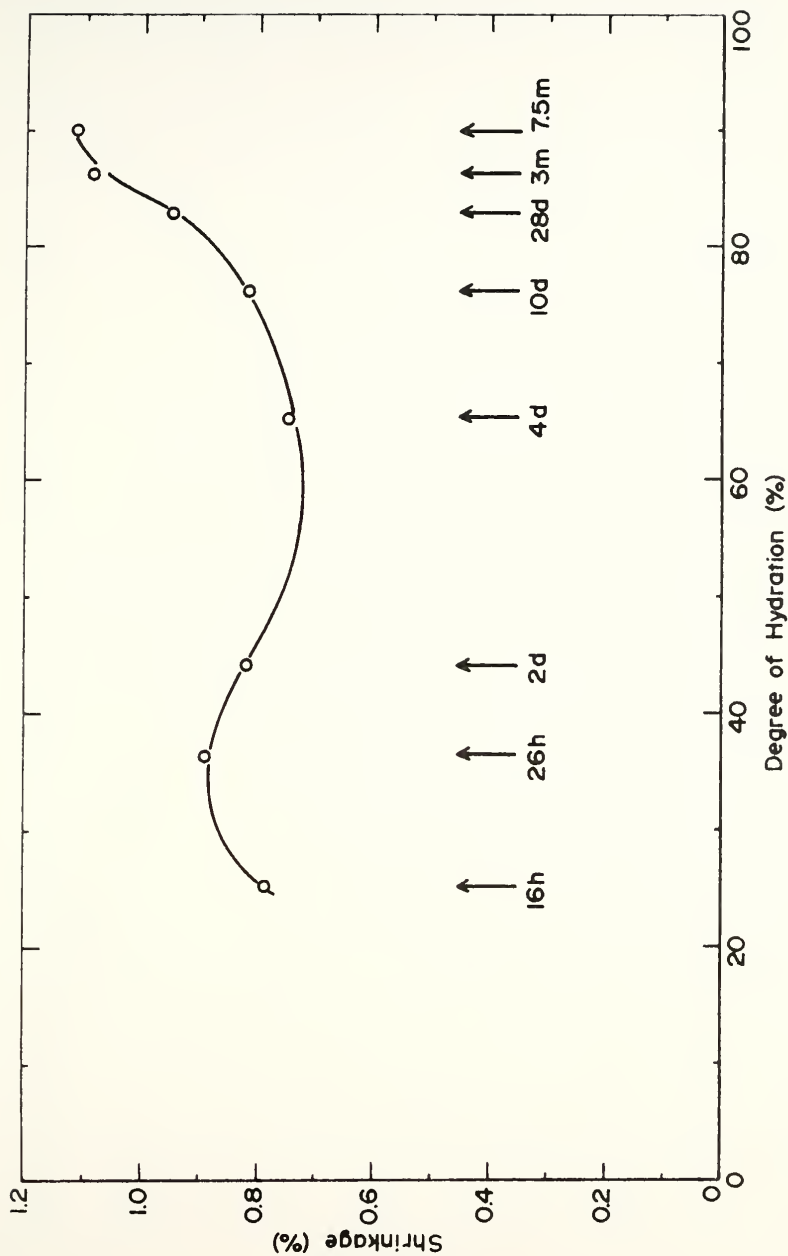


Figure 56 - Shrinkage of Vacuum Oven-Dried Cement Pastes at Various Stages of Cement Hydration (Retarder L)

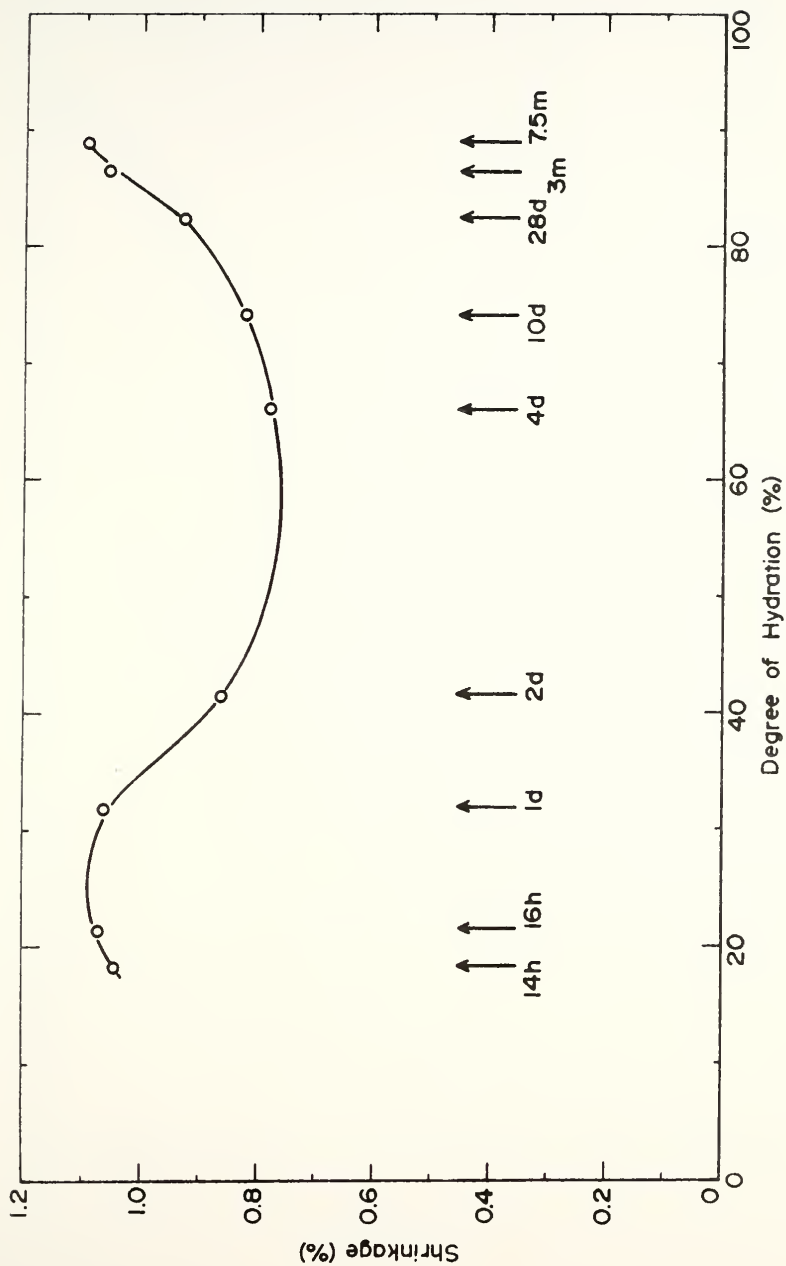


Figure 57 - Shrinkage of Vacuum Oven-Dried Cement Pastes at Various Stages of Cement Hydration (Retarder A)

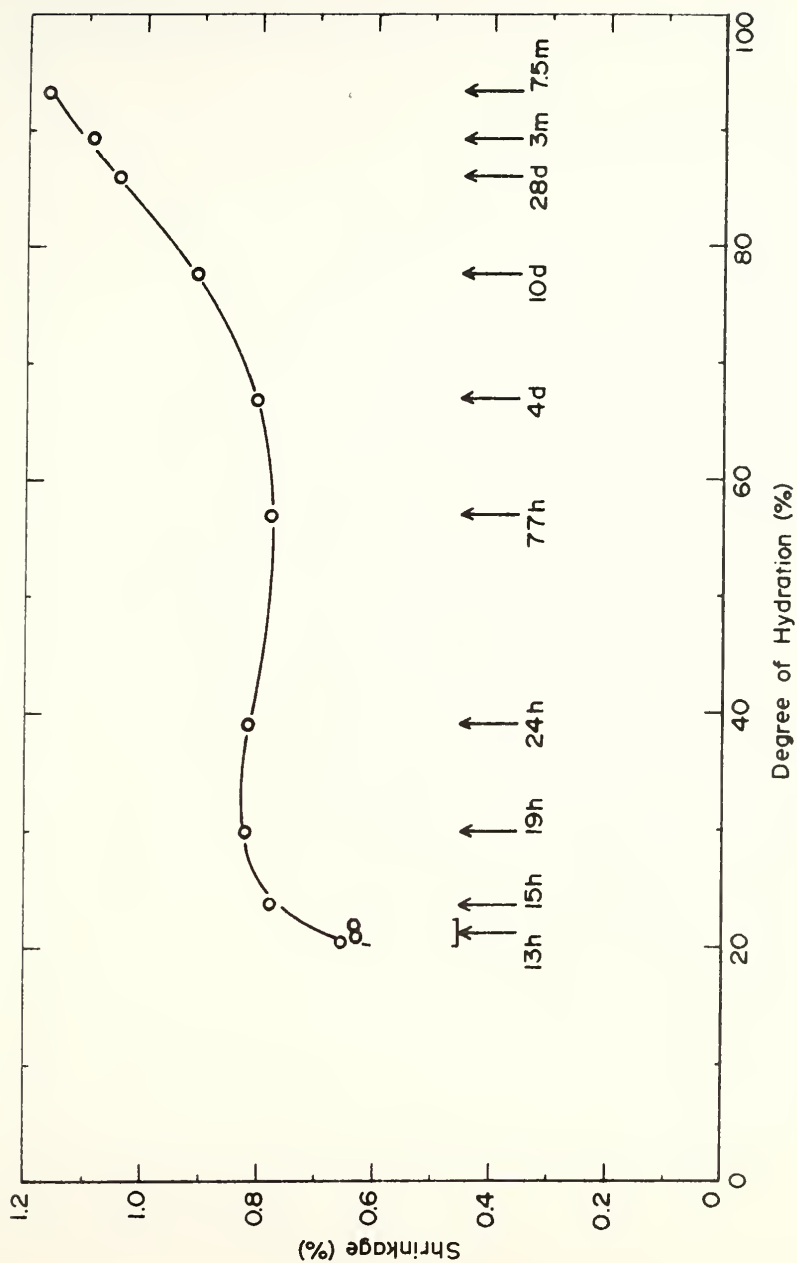


Figure 58 - Shrinkage of Vacuum Oven-Dried Cement Pastes at Various Stages of Cement Hydration (Retarder S)

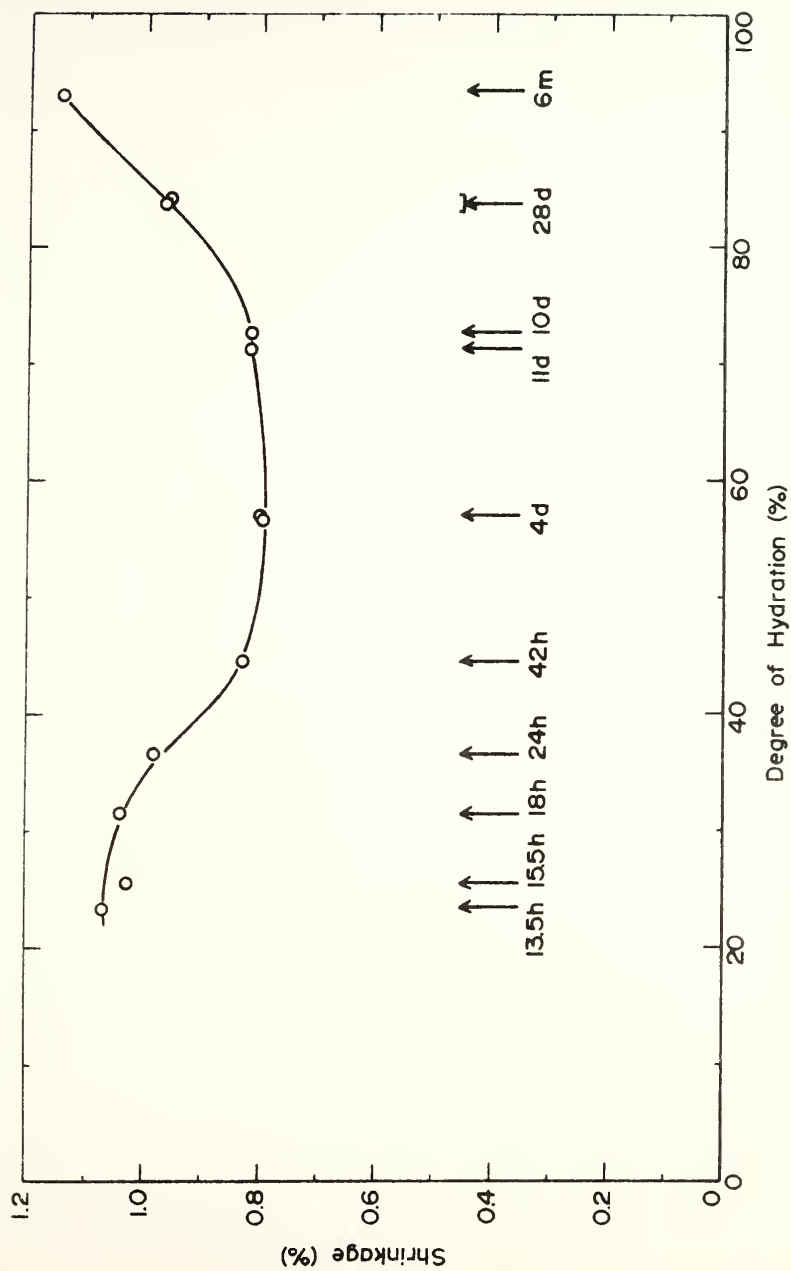


Figure 59 - Shrinkage of Vacuum Oven-Dried Cement Pastes at Various Stages of Cement Hydration (Glycolic Acid)

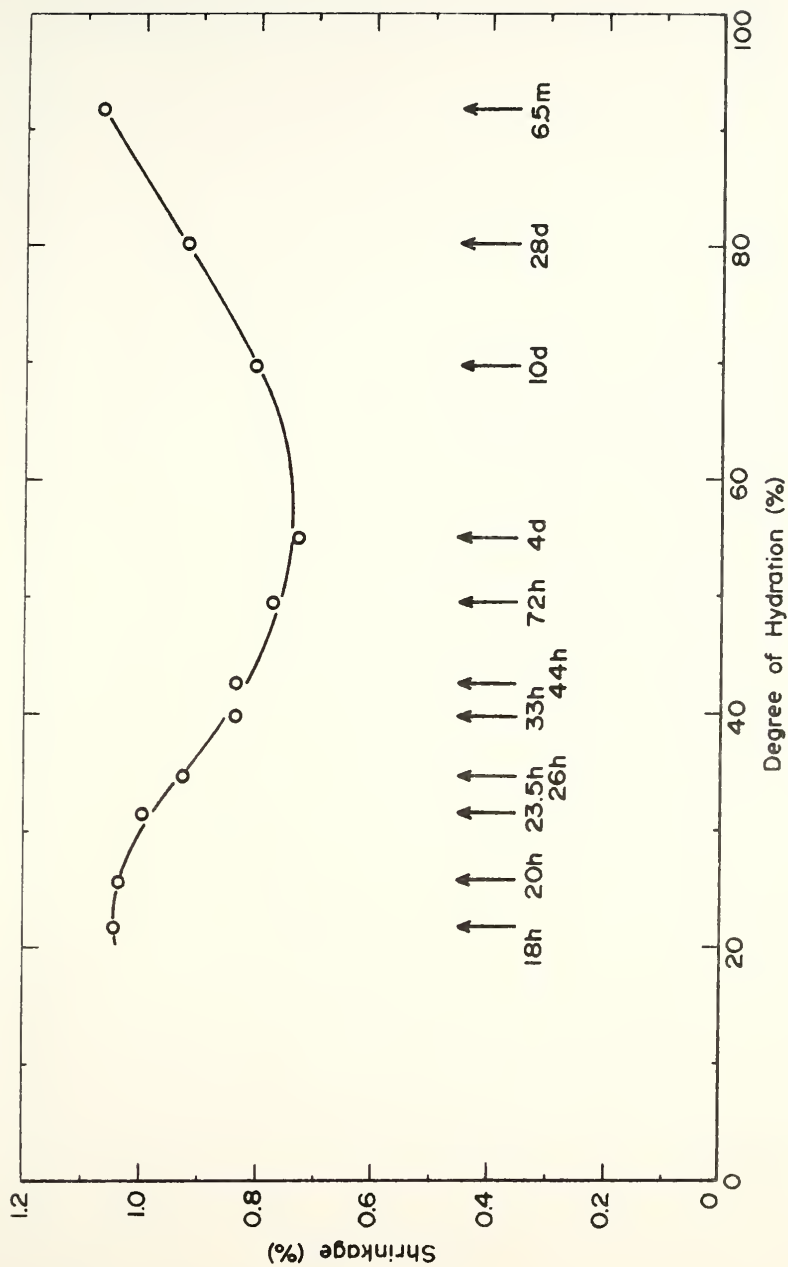


Figure 60 - Shrinkage of Vacuum Oven-Dried Cement Pastes at Various Stages of Cement Hydration (Sucrose)

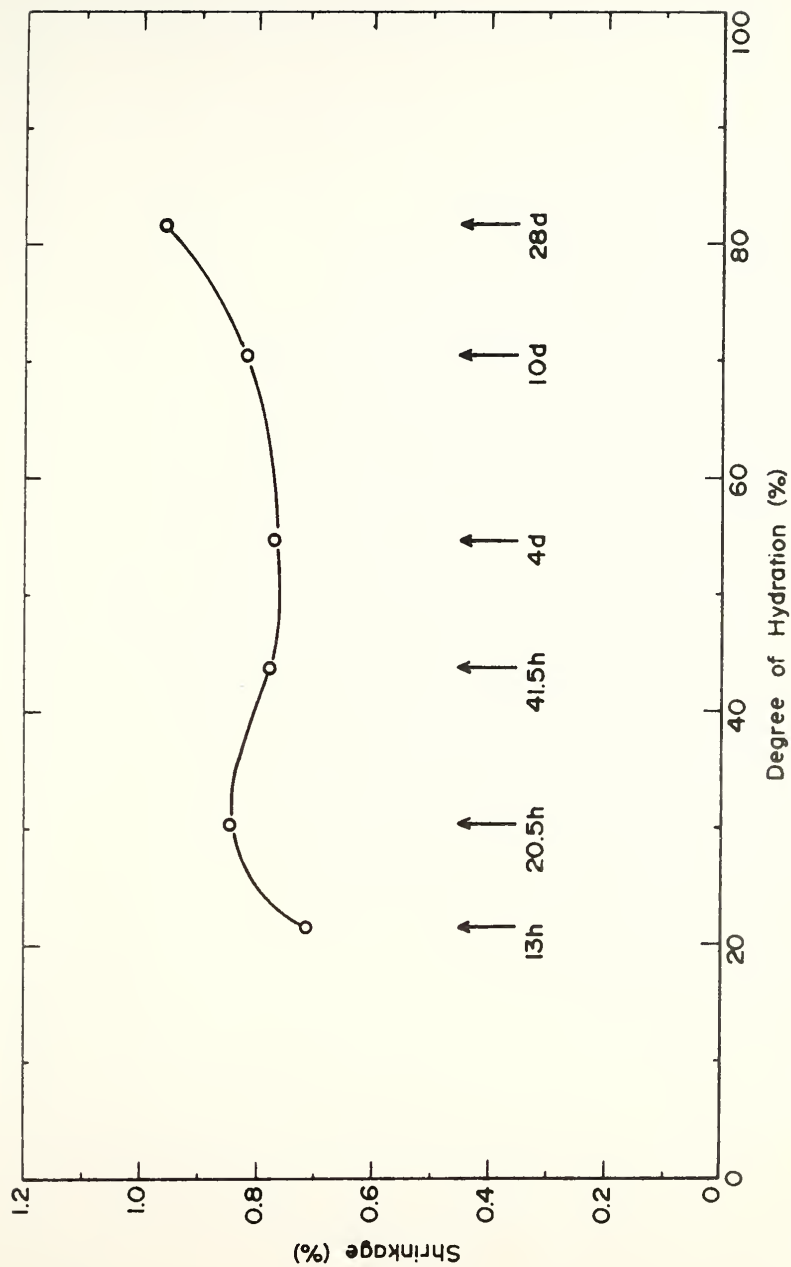


Figure 61 - Shrinkage of Vacuum Oven-Dried Cement Pastes at Various Stages of Cement Hydration (3-Hydroxy-2-Butanone)

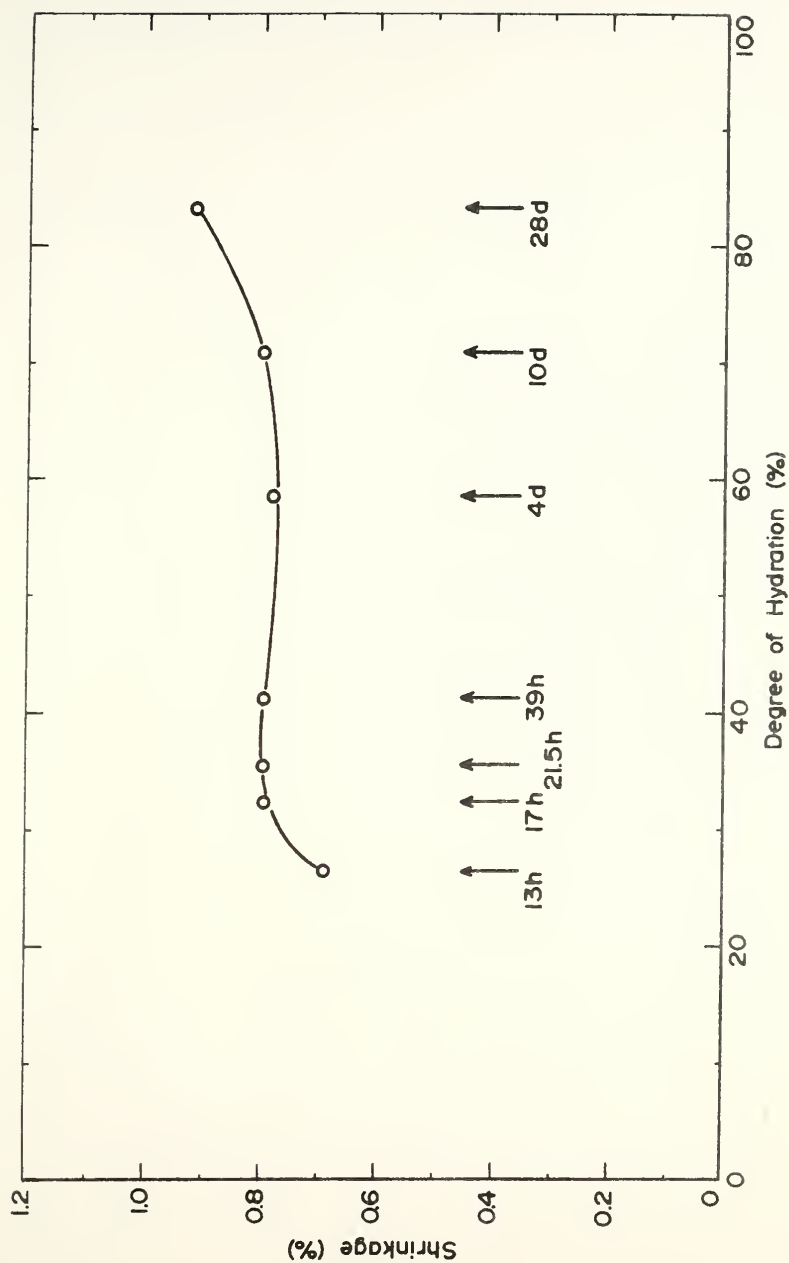


Figure 62 - Shrinkage of Vacuum Oven-Dried Cement Pastes at Various Stages of Cement Hydration (Hydroquinone)

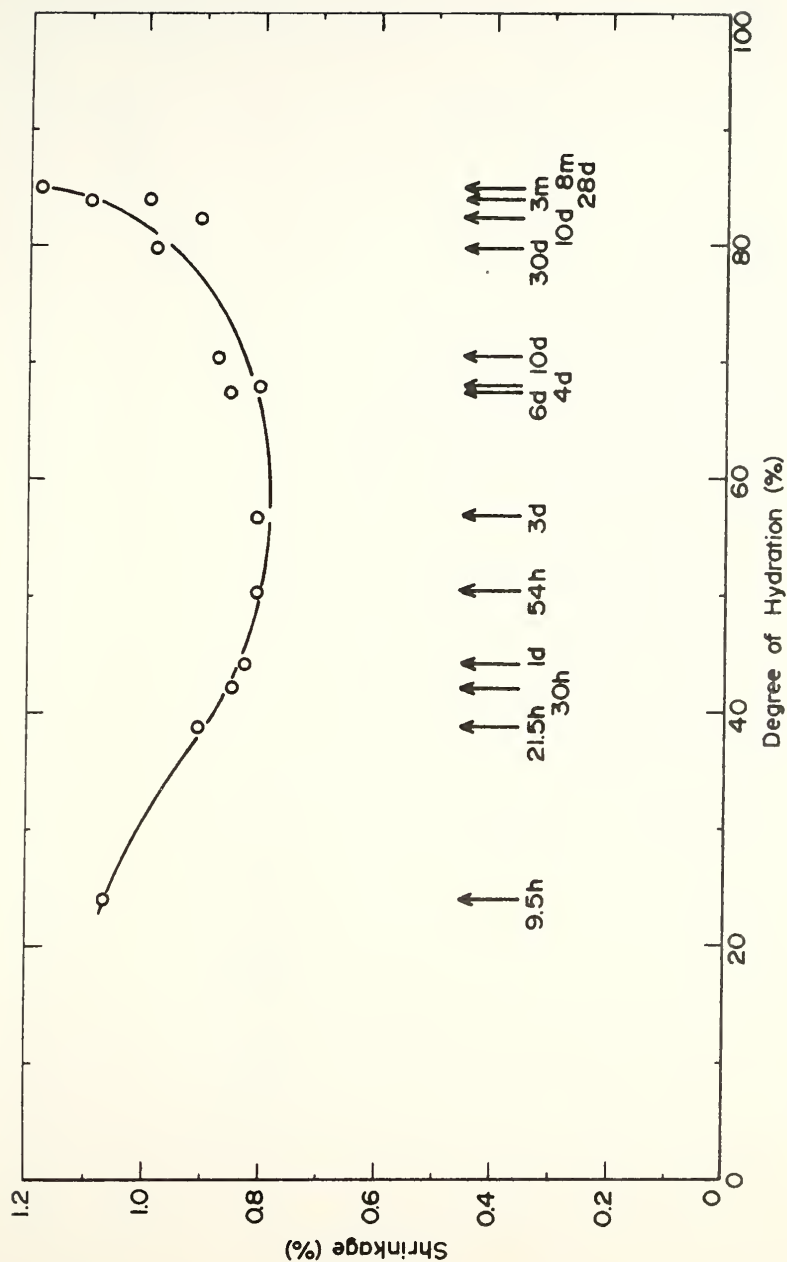


Figure 63 - Shrinkage of Vacuum Oven-Dried Cement Pastes at Various Stages of Cement Hydration ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$)

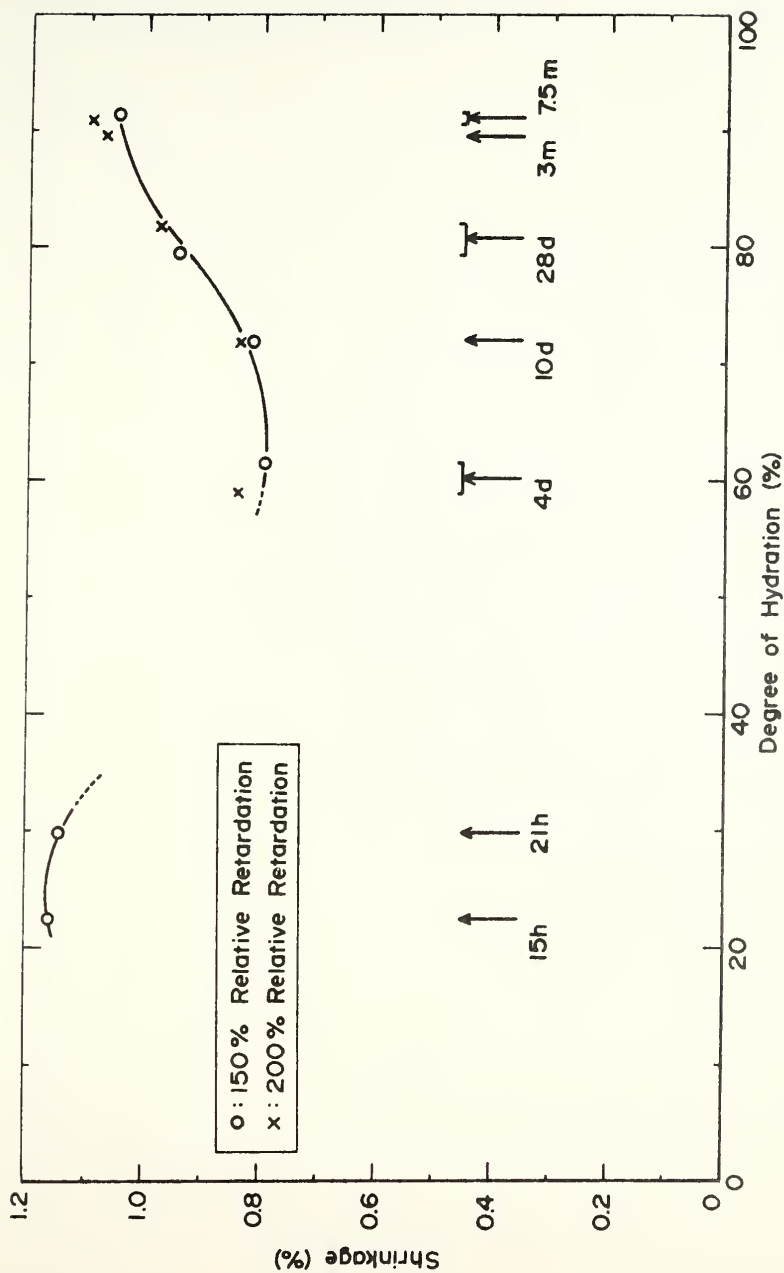


Figure 64 - Shrinkage of Vacuum Oven-Dried Cement Pastes at Various Stages of Cement Hydration (Effect of Concentrations of Citric Acid)

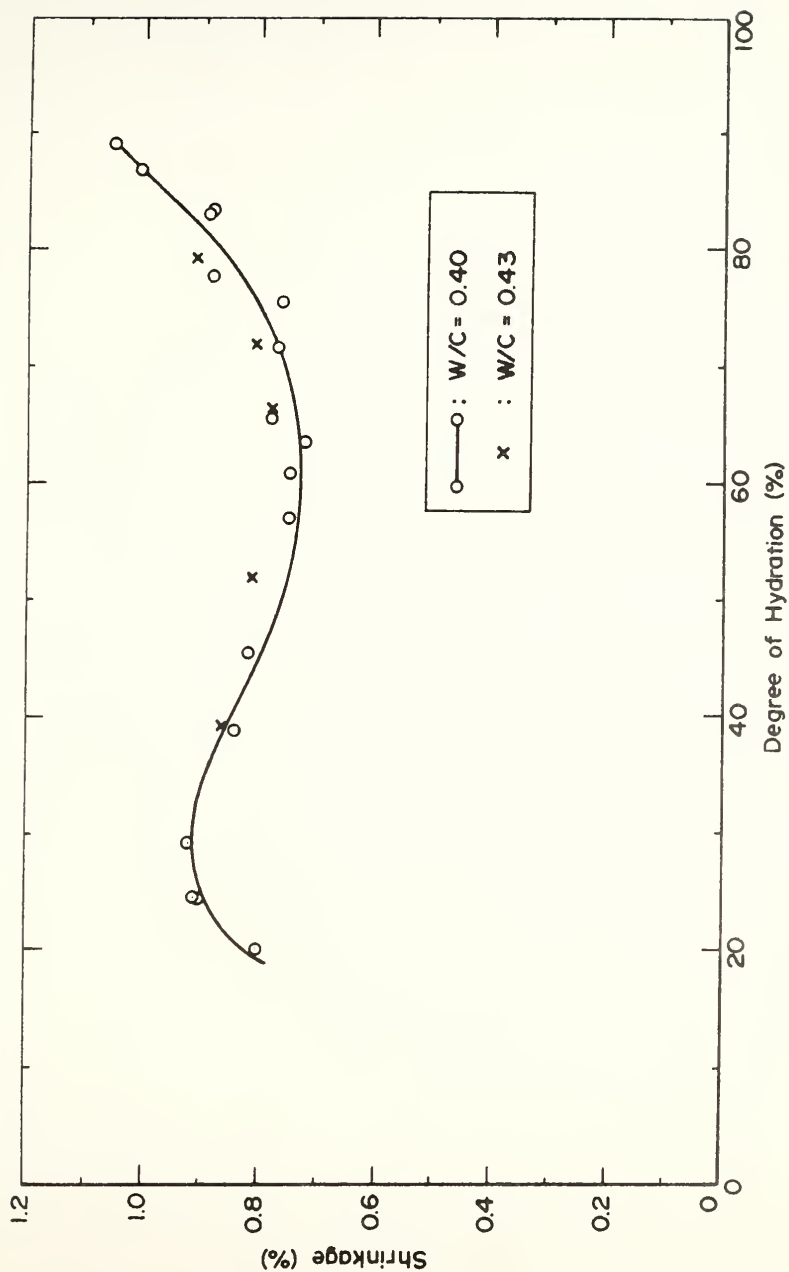


Figure 65 - Shrinkage of Vacuum Oven-Dried Cement Pastes at Various Stages of Cement Hydration (Effect of Water-Cement Ratio)

VITA

VITA

Yasuhiko Yamamoto was born on May 1, 1943 in Korea. He is a citizen of Japan.

After completing early education at Kofu First High School in Yamanashi prefecture, he entered Yamanashi University where he received B.S.C.E. degree in March 1966.

In April 1966, he became a graduate student of University of Tokyo and received M.S.C.E. degree in March 1968. He continued his study at the same university toward Doctor of Science degree until he came to the U.S.A. to study at Purdue University in September 1969.

